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ORDER–DISORDER TRANSFORMATION IN LIQUID CRYSTALS BY GAS–LIQUID CHROMATOGRAPHY *

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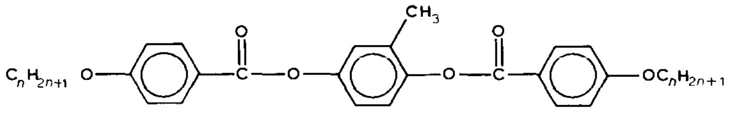
ABSTRACT

The infinite dilution activity coefficients of C_8 aromatics were measured in the nematic phase and isotropic phase of *p*-(*o*-methylphenylene)-bis-*n*-alkoxybenzoate (MPBRB) over a wide temperature range. Two reduced variables σ and τ were introduced to treat the data. It is found that the relationship between σ and τ is consistent with the principle of corresponding states.

INTRODUCTION

It is well known that in the gas–liquid chromatographic (GLC) separation of *meta*- and *para*-disubstituted benzenes, the nematic liquid crystals show pronounced retention of the more linear *para* isomers [1]. There has been a great deal of research reported on the use of *p*-(*o*-methylphenylene)-bis-alkoxybenzoate (MPBRB) liquid crystals as the stationary phase in GLC to analyse aromatic mixtures. It is therefore evident that detailed solution thermodynamic studies are needed in order fully to expose the mechanism of the retention of aromatic solutes in the MPBRB liquid crystals. In this article, the infinite dilution activity coefficients γ_i of the C_8H_{10} aromatic isomers (ethylbenzene and xylenes) were measured in the nematic phases and isotropic phases of MPBRB over a wide temperature range by GLC. Two parameters, σ and τ, were introduced to treat the data, and the change of short-range order of liquid crystal with temperature was discussed.

The studied MPBRB homologous series have the general formula



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where, $n = 6$ ($MPBH_xB$), n = 7 ($MPBH_pB$), $n = 8$ (MPBOB), or $n = 10$ (MPBDB).

EXPERIMENTAL

The MPBRB liquid crystalline substances were supplied by Shanghai Chemical Products. The transition points were measured by a DuPont 1090B differential scanning calorimeter (DSC) and the results are shown, with the literature values, in Table 1.

The solutes (AR products) were used without further purification.

A gas chromatograph, modified for the accurate measurement of pressure at the column inlet and for control of the column temperature to $+0.1\,°C$ at $120\,°C$ was used. The procedure followed to obtain accurate retention volumes is described elsewhere [2].

The activity coefficient, γ_i, was calculated using the expression

$$\ln \gamma_i = \ln \frac{273.2R}{V_g P_1^0 M_2} - \frac{P_1^0}{RT}(B_{11} - V_1)$$

where V_g is the specific retention volume of solute, P_1^0, V_1, and B_{11} are the vapour pressure, molar volume and second virial coefficient of the solute, and M_2 is the molar mass of the solvent.

TABLE 1

Transition temperature of MPBRB obtained by DSC and GLC

$MPBH_xB$	Literature value	Solid $\overset{87.9\,°C}{\rightleftharpoons}$ Nematic $\overset{171.8\,°C}{\rightleftharpoons}$ Isotropic
	DSC	Solid $\overset{88.0\,°C}{\rightleftharpoons}$ Nematic $\overset{172.0\,°C}{\rightleftharpoons}$ Isotropic
	GLC	Nematic $\overset{172.0\,°C}{\rightleftharpoons}$ Isotropic
$MPBH_pB$	Literature value	Solid $\overset{84.0\,°C}{\rightleftharpoons}$ Nematic $\overset{159.0\,°C}{\rightleftharpoons}$ Isotropic
	DSC	Solid $\overset{83.7\,°C}{\rightleftharpoons}$ Nematic $\overset{160.0\,°C}{\rightleftharpoons}$ Isotropic
	GLC	Nematic $\overset{161.0\,°C}{\rightleftharpoons}$ Isotropic
MPBOB	Literature value	Solid $\overset{72.0\,°C}{\rightleftharpoons}$ Nematic $\overset{156.0\,°C}{\rightleftharpoons}$ Isotropic
	DSC	Solid $\overset{72.6\,°C}{\rightleftharpoons}$ Nematic $\overset{156.2\,°C}{\rightleftharpoons}$ Isotropic
	GLC	Nematic $\overset{158.0\,°C}{\rightleftharpoons}$ Isotropic
MPBDB	Literature value	Solid $\overset{80.0\,°C}{\rightleftharpoons}$ Nematic $\overset{144.0\,°C}{\rightleftharpoons}$ Isotropic
	DSC	Solid $\overset{80.3\,°C}{\rightleftharpoons}$ Nematic $\overset{145.0\,°C}{\rightleftharpoons}$ Isotropic
	GLC	Nematic $\overset{143.0\,°C}{\rightleftharpoons}$ Isotropic

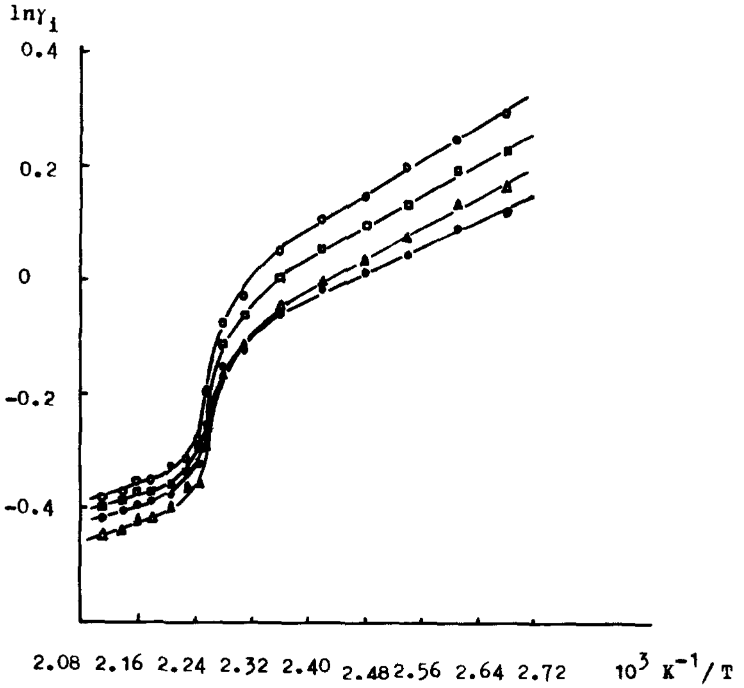

Fig. 1. Plot of ln γ_i against $1/T$ in $MPBH_xB$. ○, Ethylbenzene; □, *m*-xylene; △, *o*-xylene; ●, *p*-xylene.

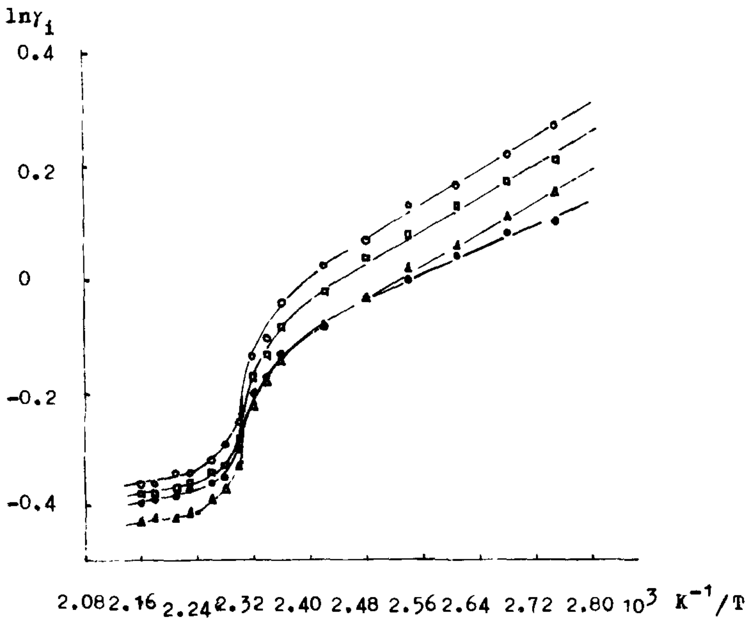

Fig. 2. Plot of ln γ_i against $1/T$ in $MPBH_pB$. ○, Ethylbenzene; □, *m*-xylene; △, *o*-xylene; ●, *p*-xylene.

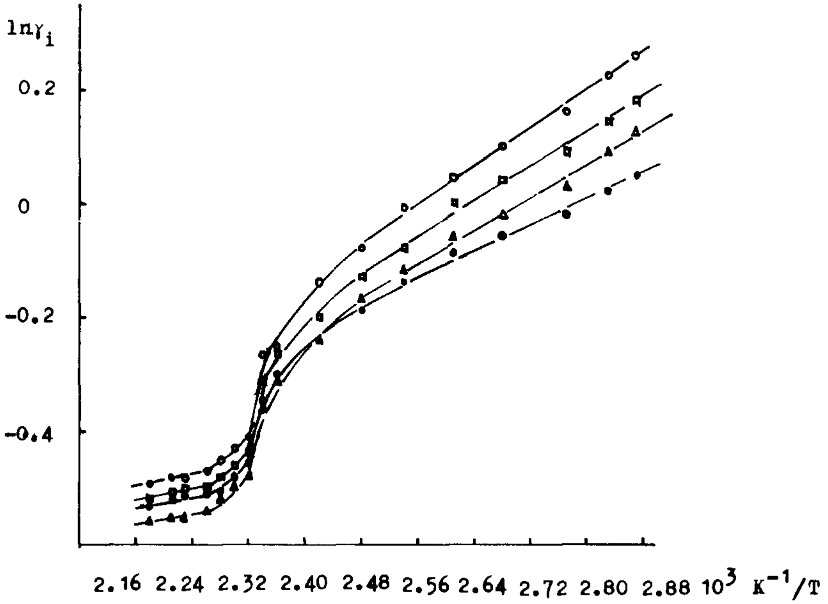

Fig. 3. Plot of ln γ_i against $1/T$ in MPBOB. ○, Ethylbenzene; □, *m*-xylene; △, *o*-xylene; ●, *p*-xylene.

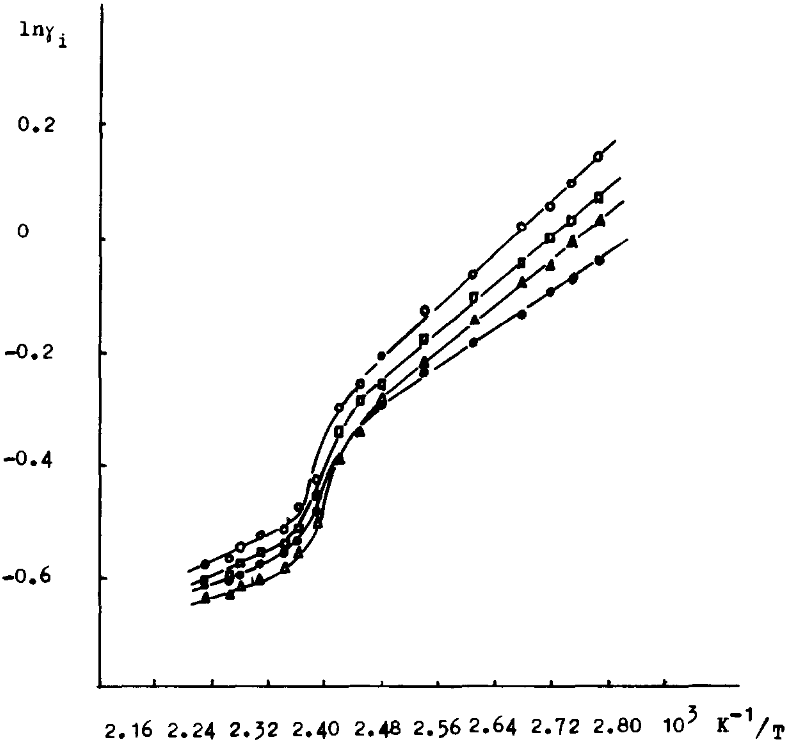

Fig. 4. Plot of ln γ_i against $1/T$ in MPBDB. ○, Ethylbenzene; □, *m*-xylene; △, *o*-xylene; ●, *p*-xylene.

RESULTS

Figures 1–4 are the ln γ_i vs. $1/T$ plots. There is a discontinuity in the slope of the plots at the nematic–isotropic liquid transition temperature. The points of sudden change are also shown in Table 1.

DISCUSSION

As shown in Figs. 1–4, in the nematic phase (at high temperature, on the right of the figures) the activity coefficient of *p*-xylene is the smallest of the aromatic isomers studied. It reflects that the more linear isomer *p*-xylene has the more capability accommodated in the ordered nematic domain. A relative activity coefficient

$$\alpha = \frac{\gamma_i}{\gamma_{p\text{-}xy}}$$

can be introduced to express the selectivity of separation with respect to *p*-xylene. The α values with temperatures are listed in Tables 2–5. For comparison, the values of α in dinonyl phthalate, a non-liquid crystal substance, are listed in Table 6. Observing the trends of α in MPBRB and in dinonyl phthalate with the changes of temperature, it can be seen that, as

TABLE 2

Values of τ, α and σ of solutes in $MPBH_xB$

$t/°C$	τ	α			σ		
		Ethylbenzene	*o*-Xylene	*m*-Xylene	Ethylbenzene	*o*-Xylene	*m*-Xylene
88	0.000	1.20	1.05	1.12	1.00	1.00	1.00
100	0.143	1.18	1.04	1.11	0.88	0.88	0.91
110	0.262	1.17	1.04	1.10	0.81	0.88	0.82
120	0.381	1.16	1.03	1.09	0.75	0.75	0.73
130	0.500	1.14	1.02	1.08	0.63	0.63	0.64
140	0.619	1.13	1.02	1.08	0.57	0.63	0.64
150	0.738	1.12	1.01	1.07	0.50	0.50	0.55
160	0.857	1.11	1.01	1.06	0.44	0.50	0.45
165	0.917	1.09	1.00	1.05	0.31	0.38	0.36
170	0.976	1.06	0.99	1.04	0.13	0.25	0.27
172	1.00	1.06	0.98	1.03	0.06	0.13	0.18
175	1.04	1.05	0.97	1.02	0.06	0	0.09
180	1.10	1.05	0.97	1.02	0	0	0.09
185	1.15	1.04	0.97	1.02	0	0	0.09
190	1.21	1.04	0.97	1.02	0	0	0.09
195	1.27	1.04	0.97	1.01	0	0	0
200	1.33	1.04	0.97	1.01	0	0	0

TABLE 3

Values of τ, α and σ of solutes in $MPBH_pB$

$t/°C$	τ	α			σ		
		Ethylbenzene	*o*-Xylene	*m*-Xylene	Ethylbenzene	*o*-Xylene	*m*-Xylene
84	0	1.20	1.06	1.12	1.00	1.00	1.00
90	0.078	1.18	1.06	1.12	0.88	1.00	1.00
100	0.208	1.16	1.04	1.10	0.75	0.80	0.82
110	0.338	1.14	1.03	1.09	0.63	0.70	0.73
120	0.468	1.12	1.01	1.08	0.50	0.50	0.64
130	0.597	1.11	1.00	1.07	0.44	0.40	0.54
140	0.727	1.10	1.00	1.06	0.38	0.40	0.45
150	0.857	1.08	0.99	1.04	0.25	0.30	0.27
155	0.922	1.07	0.98	1.03	0.19	0.20	0.18
158	0.961	1.06	0.97	1.02	0.13	0.10	0.09
161	1.00	1.06	0.97	1.02	0.06	0.10	0.09
165	1.05	1.05	0.97	1.02	0	0	0
170	1.12	1.04	0.96	1.01	0	0	0
175	1.18	1.04	0.96	1.01	0	0	0
180	1.25	1.04	0.96	1.01	0	0	0
185	1.31	1.04	0.96	1.01	0	0	0
191	1.38	1.04	0.96	1.01	0	0	0

TABLE 4

Values of τ, α and σ of solutes in MPBOB

$t/°C$	τ	α			σ		
		Ethylbenzene	*o*-Xylene	*m*-Xylene	Ethylbenzene	*o*-Xylene	*m*-Xylene
72	0	1.24	1.08	1.14	1.00	1.00	1.00
75	0.035	1.23	1.08	1.14	0.95	1.00	1.00
80	0.093	1.22	1.07	1.13	0.90	0.91	0.92
90	0.209	1.20	1.06	1.12	0.80	0.82	0.85
100	0.326	1.18	1.04	1.10	0.70	0.64	0.69
110	0.442	1.15	1.03	1.09	0.55	0.55	0.62
120	0.558	1.13	1.02	1.08	0.45	0.45	0.54
130	0.674	1.12	1.02	1.06	0.40	0.45	0.38
140	0.791	1.11	1.01	1.05	0.35	0.36	0.31
150	0.907	1.09	0.99	1.05	0.25	0.18	0.31
154	0.953	1.08	0.98	1.03	0.20	0.09	0.15
158	1.00	1.05	0.98	1.02	0.05	0.09	0.08
161	1.03	1.05	0.98	1.02	0.05	0.09	0.08
165	1.08	1.05	0.97	1.02	0.05	0	0.08
170	1.14	1.04	0.97	1.01	0	0	0
175	1.20	1.04	0.97	1.01	0	0	0
180	1.26	1.04	0.97	1.01	0	0	0
185	1.31	1.04	0.97	1.01	0	0	0

TABLE 5

Values of τ, α and σ of solutes in MPBDB

$t/°\mathrm{C}$	τ	α			σ		
		Ethylbenzene	*o*-Xylene	*m*-Xylene	Ethylbenzene	*o*-Xylene	*m*-Xylene
80	0	1.21	1.08	1.13	1.00	1.00	1.00
85	0.079	1.20	1.07	1.12	0.94	0.90	0.91
90	0.154	1.18	1.06	1.11	0.81	0.80	0.82
95	0.238	1.17	1.06	1.10	0.75	0.80	0.73
100	0.317	1.16	1.05	1.09	0.69	0.70	0.64
110	0.476	1.14	1.04	1.08	0.56	0.60	0.54
120	0.635	1.12	1.02	1.06	0.44	0.40	0.36
130	0.794	1.10	1.01	1.06	0.31	0.30	0.36
135	0.873	1.09	1.01	1.05	0.25	0.30	0.27
140	0.952	1.09	1.00	1.05	0.25	0.20	0.27
143	1.00	1.07	0.99	1.04	0.12	0.10	0.18
145	1.03	1.06	0.99	1.03	0.06	0.10	0.09
150	1.11	1.06	0.98	1.02	0.06	0	0
155	1.19	1.05	0.97	1.02	0	0	0
160	1.27	1.05	0.97	1.02	0	0	0
165	1.35	1.05	0.98	1.02	0	0	0
170	1.43	1.05	0.98	1.02	0	0	0

the temperature is increased, the value of α of each solute in dinonyl phthalate is almost invariable but the α value of each solute in any member of the MPBRB series is apparently decreased and approaches a common limit, which is close to the value in dinonyl phthalate.

In order to describe the above behaviour, we introduce empirically two reduced variables which are defined as

$$\tau = \frac{T - T_{\mathrm{FN}}}{T_{\mathrm{NI}} - T_{\mathrm{FN}}}$$

$$\sigma = \frac{\alpha - \alpha_{\infty}}{\alpha_{\mathrm{FN}} - \alpha_{\infty}}$$

where T_{FN} is the crystal–nematic transition temperature, T_{NI} is the

TABLE 6

Values of α of solutes in dinonylphthalate

$t/°\mathrm{C}$	Ethylbenzene	*o*-Xylene	*m*-Xylene
80	1.04	0.97	1.01
90	1.03	0.97	1.01
100	1.03	0.98	1.01
110	1.02	0.97	1.02
120	1.02	0.97	1.01

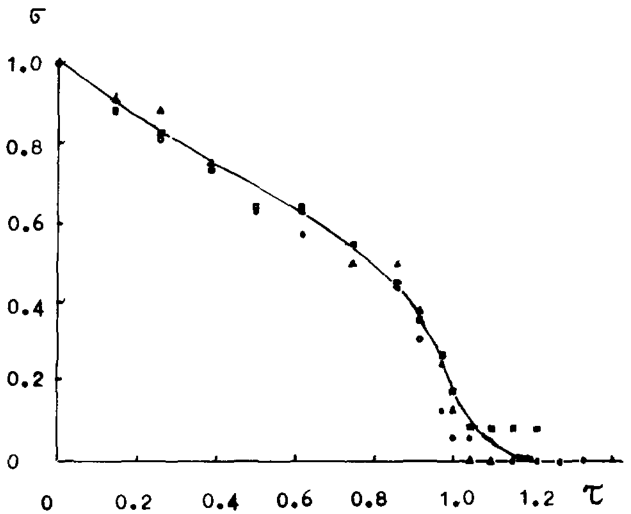

Fig. 5. Plot of ln σ against τ in MPBH$_x$B. ○, Ethylbenzene; □, *m*-xylene; △, *o*-xylene.

nematic–isotropic transition temperature, α_{FN} is the value of α at T_{FN} and α_∞ is the limiting value at high temperature. The values of σ and τ are shown in Tables 2–5. It is found that the relationship between σ and τ is consistent with the principle of corresponding states, that is to say that all the σ and τ values belonging to the same member of the MPBRB series lie on a smooth curve (see Figs. 5–8). It can be safely assumed that, in the isotropic region of each MPBRB, the intermolecular interactions between solvent and solute all have a conformal potential (i.e. the same type of

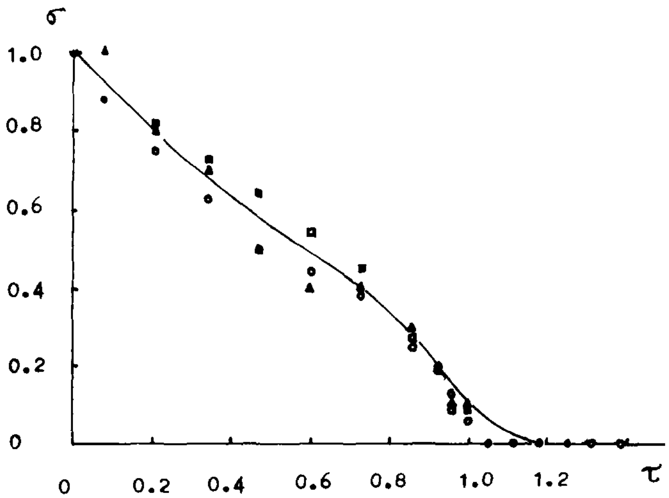

Fig. 6, Plot of ln σ against τ in MPBH$_p$B. ○, Ethylbenzene; □, *m*-xylene; △, *o*-xylene.

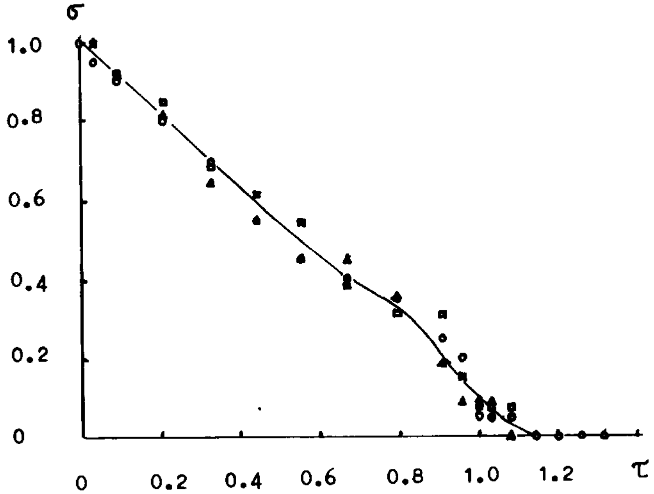

Fig. 7. Plot of ln σ against τ in MPBOB. ○, Ethylbenzene; □, *m*-xylene; △, *o*-xylene.

potential energy curve), yet have a conformal potential in the nematic region with the exception of *p*-xylene solute.

It is also found from the σ vs. τ plots that, as the temperature increases to T_{NI}, the value of σ decreases rather sharply. We suggest that the variable σ has some character similar to the short-range orientational parameter in order–disorder transformations which takes the value unity in the completely ordered state and zero in the completely disordered state) and which falls with rising temperature, and approaches zero at high temperature.

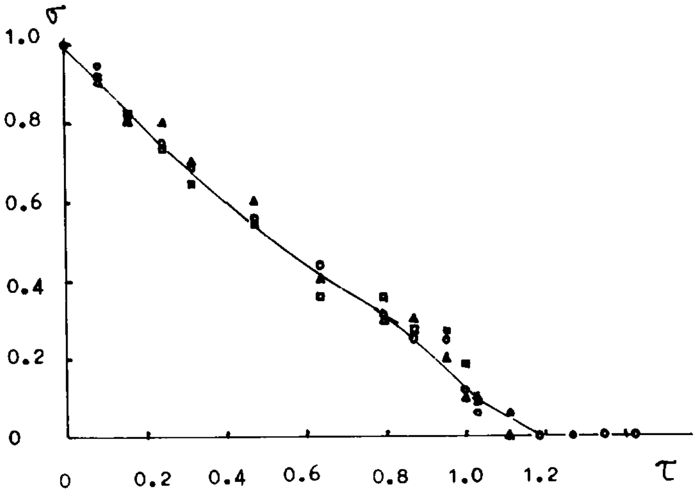

Fig. 8. Plot of ln σ against τ in MPBDB. ○, Ethylbenzene; □, *m*-xylene; △, *o*-xylene.

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