Relationship Between the Preferential Adsorption Coefficient and Polymer Molecular Dimensions in Mixed Solvents

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SUMMARY

In this paper a relationship between the preferential adsorption coefficient and polymer molecular dimensions is proposed

$$\lambda \frac{<s^2>^{3/2}}{M} = \lambda_\infty \frac{<s^2>^{3/2}}{M} + A(\frac{<s_0^2>}{M})^{3/2}$$

This relationship is found to be valid for all polymers in good theta solvents and for any molecular weight.

INTRODUCTION

In two recent papers (KATIME et al.1979 and KATIME,AMO) we described a new plot of preferential adsorption co-efficient as a function of intrinsic viscosity which gives a straight line and enables to find λ_∞ and A. In this paper another equation is given relating in a sim-ple way the preferential adsorption coefficient, λ, to the mean square radius of gyration, $<s^2>$, and the mole-cular weight M and allows to calculate λ_∞ and A with precision, independently of the thermodynamical condi-tions, in which the system is found. The results obtained are compared with the ones calculated with Dondos-Benoit's equation (DONDOS, BENOIT 197o).

EXPERIMENTAL PROCEDURES AND RESULTS

Poly(methyl methacrylate) was obtained by anionic poly-

merization in THF solution initiated with butyllithium
(KATIME,RAMIRO VERA 1972). The polymer was reprecipita-
ted from benzene solution with methanol. The fractions
were obtained by gradual precipitation of the polymer
from the benzene solution with isopropanol.

Molecular weight determinations by both light scatter-
ing and osometry on several fractions showed that

$$\overline{M}_w/\overline{M}_n < 1.3.$$

Dioxane was a chemically pure commercial product, redis-
tilled on a 42 plate laboratory column prior to use: its
purity was checked chromatographically.

Solvent mixtures of dioxane/methanol were made up by vo-
lume. The refractive indices of the solvents and of the
binary solvent mixtures were measured with an Abbé ref-
ractometer at 298 K.

Molecular weight distributions have been evaluated by
GPC.

The intensity of scattered light was measured at 298 K
with a PGD FICA apparatus over the angular range 3o-15o$^{\circ}$.
We used an unpolarized primary beam with a wavelength of
546 nm. Reduced scattered intensities for zero concen-
trations and zero angle were obtained by the Zimm method
(ZIMM 1948). Before measurements the solutions were freed
from dust by centrifugation for 2 hrs in a Sorvell prepa-
rative ultracentrifuge.

A Brice-Phoenix differential refractometer Model BP-2oooV
equipped with a special glass cell R 1o1 was used for
measurements of refractive increments at constant sol-
vent composition. All measurements were made using green
mercury line (546 nm). Aqueous solutions of sodium chloride

at 298 K were used for the calibration of the differen-
tial refractometer (KRUISS 1936).

Table 1 shows the preferential adsorption coefficient,
λ, and mean square radius of gyration, $<s^2>$, as a func-
tion of molecular weight, M, and composition of the bi-
nary mixture, u_2.

DISCUSSION

According to Dondos and Benoit

$$\lambda = \lambda_\infty + \frac{A}{M^{1/2} \alpha^3} . \tag{1}$$

TABLE 1

Preferential adsorption coefficient, λ, and mean
square radius of gyration, $<s^2>$, of PMMA in the binary
mixture dioxane(1)/methanol(2).

| | λ ml/g | | | | $<s^2>.10^{11}$ cm^2 | | | |
$M.10^{-6}$	20.	30.	40.	50.	20.	30.	40.	50.
0.435	–	0.102	0.132	–	–	0.90	0.78	–
0.616	-0.011	–	–	0.129	1.47	–	–	0.82
1.12	-0.005	0.097	0.131	0.106	3.08	2.92	2.74	2.50
2.03	-0.001	0.093	0.127	0.103	6.94	6.86	6.05	4.72
2.40	-0.0	0.093	0.127	0.103	8.46	7.11	6.72	5.04

where λ_∞ is the limiting value of the preferential ad-
sorption coefficient, A a constant and α^3 the linear ex-
pansion coefficient of the polymer. Assuming $\alpha^3 =$
$(<s^2>/<s^2>_o)^{3/2}$ in Equation (1), we obtain

$$\lambda \left(\frac{<s^2>^{3/2}}{M} \right) = \lambda_\infty \left(\frac{<s^2>^{3/2}}{M} \right) + A \left(\frac{<s_o^2>}{M} \right)^{3/2} \tag{2}$$

where $<s^2>$ and $<s_0^2>$ are, the perturbed and unperturbed mean square radius of gyration of the polymer. Evidently, a plot of $\lambda(<s^2>^{3/2}/M)$ versus $<s^2>^{3/2}/M$ should give a straight line, according to the above theoretical relation, being the slope λ_∞ and the intercept equal to $A(<s_0^2>/M)^{3/2}$. The obtained result using the equation (2) for PMMA(3)/dioxane(1)/methanol(2) system at several compositions of the binary mixture can be seen in Figure 1. We notice that, for all cases the experimental points fall indeed on a straight line, confirming the above relation. This confirms that the preferential adsorption parameter, the molecular weight and the dimensions of the macromolecule are closely related. This fact was expected because several papers on ternary systems have proved that the intramolecular

parameter K_θ depends on the composition of the binary mixture (DONDOS, BENOIT 1968, 1977 and KATIME et al. 1975). On the other hand, Equation (2) assumes neither an aproximation nor a limitation while Equation (1) can be only applied in a strict way when the system is found in ideal or theta conditions in which the linear expansion coefficient is equal to unity. If this is not so it is necessary to suppose that $\alpha^3 \rightarrow 1$. This approximation must not alterate in any case the values of λ_∞, but the value of the parameter A obtained from the intercept changes. As can be seen in Table 2, the A values obtai-

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TABLE 2

Values of A and λ_∞ obtained using Equations (1) and (2).

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u_2	λ_∞ ml/g		A	
	Eq.(1)	Eq.(2)	Eq.(1)	Eq.(2)
20.0	0.011	0.003	−17.3	−24.0
30.0	0.085	0.089	10.9	11.0
40.0	0.122	0.125	7.2	7.7
50.0	0.079	0.095	35.1	37.4

ned with the equation of Dondos-Benoit are always lo-

wer than the ones calculated with the Equation (2). It is due to the fact that the values of A are divided by the linear expansion coefficient α^3. This is confirmed when plotting $\lambda M^{1/2}\alpha^3$ against $M^{1/2}\alpha^3$, because for every composition, the value of the parameter A obtained is coincident with the one calculated with Equation (2).
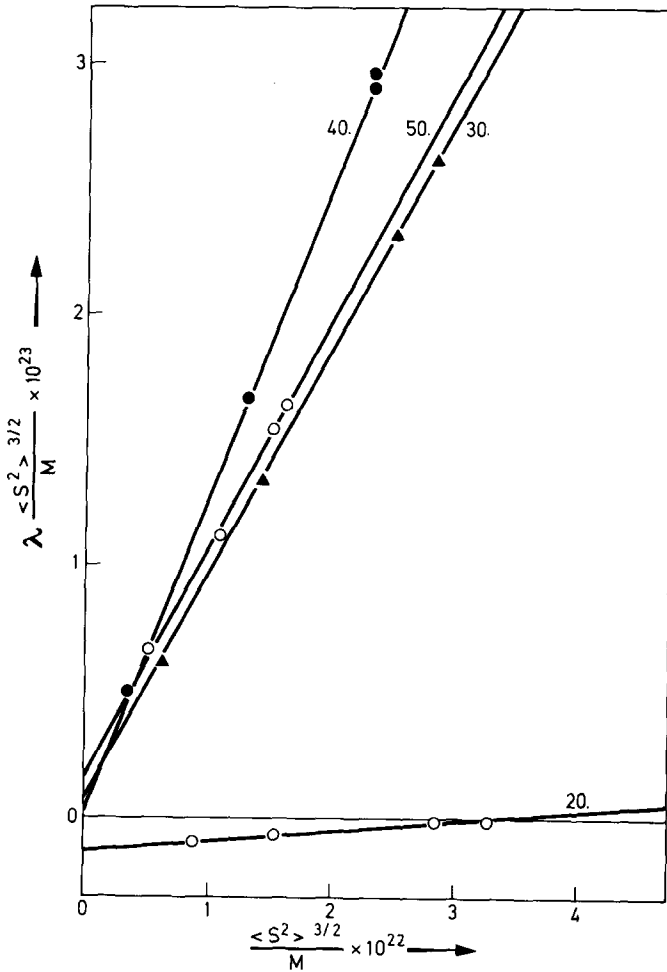

Figure 1. Plot of ($\lambda <s^2>^{3/2}/M$) as a function of ($<s^2>^{3/2}/M$) for the system PMMA(3)/dioxane(1)/ methanol(2).

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