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Relationship Between Preferential Adsorption Coefficient and Intrinsic Viscosity in Ternary Systems

Issa A. Katime and B. Amo

Departamento de Química Física, Grupo de Propiedades Termodinámicas de Macromoléculas en Disolución, Universidad del País Vasco, Apartado 644, Bilbao, Spain

SUMMARY

The relation proposed between the preferential adsorption coefficient, λ, and the intrinsic viscosity, $|\eta|$

$$\lambda|\eta| = \lambda_\infty|\eta| + AK_\theta$$

has been applied in this paper to previously published data. This equation is found to be valid in theta conditions and far away from them. The obtained results are compared to the ones calculated with the Dondos-Benoit equation.

INTRODUCTION

When a macromolecule is soluble in a binary liquid mixture it usually exhibits properties which differ from those observed for the macromolecule in a single solvent. This behaviour may be explained by supposing the macromolecule to be preferentially solvated by one of the two components of the binary liquid mixture. In the last fifteen years several groups have been studying the experimental behaviour of macromolecules in binary mixtures (HERT-STRAZIELLE 1974,1975; KATIME-STRAZIELLE 1977; KATIME et al. 1975;ZIVNY et al.1967;KATIME-VALENCIANO 1979). At the same time the theoretical basis of the phenomenon has been established, and several equations have been obtained relating the preferential adsorption coefficient, λ, to the molecular weight of the polymer, the composition of the binary mixture and the polarity of the different components of the systems (KATIME et al.1979 a, b; DONDOS-BENOIT 1978; YAMAKAWA 1967). Several empirical

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equations relating the preferential adsorption coefficient and the intrinsic viscosity $|\eta|$ of the polymer have been proposed by DONDOS (1971,1977,1978). In this paper we propose an equation from which the λ_∞ and A parameters may be evaluated in a simply way. From its application to published data, values of λ_∞ and A are obtained which can be compared to those obtained from the Dondos Benoit equation (1977).

THEORY

A short theoretical justification of the preferential adsorption phenomenon is shown here. Component 1 of the binary mixture is supposed to be preferentially adsorbed by the polymer 3. In this situation, the local concentrations, which are expressed as volume fraction, v_1, v_2, v_3, will be

$$\begin{aligned} v_1 &= (u_1 + \varepsilon)(1 - v_3) \\ v_2 &= (u_2 - \varepsilon)(1 - v_3) \end{aligned} \qquad (1)$$

where u_1 and u_2 are the volume fractions of components 1 and 2 of the binary mixture and ε the volume fraction in excess of the component 1 in the volume element dV in the macromolecular coil.

When thermodynamic equilibrium is reached between the solvent in the inside and the outside of the macromolecular coil, it is possible to express ε as a function of the interaction parameters and of the volume fractions of the components in the binary mixture

$$\varepsilon(1-v_3) = A_1(u_1)v_3 + A_2(u_1)v_3^2 + A_3(u_1)v_3^3 + \dots \qquad (2)$$

where $A_1(u_1)$, $A_2(u_1)$ and $A_3(u_1)$ are functions of the second and third derivatives of the free energy of mixing ΔG^M

$$\begin{aligned} A_1 &= M_{13}/M_{11} \\ A_2 &= -(A_1^2 M_{111} + 2A_1 M_{113} + M_{133})/2M_{11} \end{aligned}$$

where

$$M_{ij}(u_1) = (\partial^2 \Delta G^M / \partial \Phi_i \partial \Phi_j)_{v_3 \to 0}$$

and

$$M_{ijk}(u_1) = (\partial^3\Delta G^M/\partial\Phi_i\partial\Phi_j\partial\Phi_k)_{v_3\to 0}$$

Integration of Eq.(2) over the whole volume occupied by the macromolecule, assuming a Gaussian distribution of segments around the center of mass, gives

$$\rho = N(\frac{3}{2\pi R^2})^{3/2} \exp(-\frac{3r^2}{2r^2})$$

and we obtain

$$\lambda = A_1\bar{v}_3 + \frac{2C_M V_1 A_2}{\alpha^3 M^{1/2}} \qquad (3)$$

where $\bar{v}_3$ is the partial specific volume of polymer, α its expansion coefficient, and C_M a constant equal to $0.857(\bar{v}_3/N_A^2V_1)(6<s_0^2>/M)^{-3/2}$ where V_1 and $<s_o^2>$ are the molar volume of solvant 1 and the mean square radius of gyration of the polymer in theta conditions, and M its molecular weight.

Dondos y Benoit (1977) have shown that Eq.(3) may be written as

$$\lambda = \lambda_\infty + \frac{A}{\alpha^3 M^{1/2}} \qquad (4)$$

where A is a parameter describing the segment density influence on λ and λ_∞ is the preferential adsorption coefficient for an infinite molecular weight polymer.

By making $\alpha^3 = |\eta|/K_\theta M^{1/2}$ in Eq.(4) and regrouping terms, we finally obtain

$$\lambda|\eta| = \lambda_\infty|\eta| + AK_\theta \qquad (5)$$

an equation which allows us to obtain λ_∞ and A by the combination of equilibrium properties with hydrodynamic properties. The plot of $\lambda|\eta|$ against $|\eta|$, at constant binary mixture composition, will lead to a straight line with an intercept equal to AK_θ and a slope equal to λ_∞.

DISCUSSION

In order to test the validity of Eq.(4) and Eq.(5) published data for λ, $|\eta|$ and molecular weight of the ternary systems polystyrene(3)/benzene(1)/methanol(2) (DONDOS-BENOIT 1977), polystyrene(3)/CCl_4(1)/methanol(2)(DONDOS-BE

NOIT 1977) and isotactic polybutene(3)/cyclohexane(1)/n-propanol(2)(KATIME et al.1975) have been used. Each of the three systems is now discussed separately.

a) Polystyrene(3)/benzene(1)/methanol(2). Figure 1 shows the Dondos-Benoit plot and the one proposed in this paper for the polystyrene(3)/benzene(1)/methanol(2) system at 10%. It can be seen that the experimental points fit better Eq.(5). Table 1 shows the values of λ_∞ and A obtained by using the Eqs.(4) and (5). The values of the unperturbed dimensions K_θ calculated by means of the Stockmayer-Fixman equation and the values of the exponent of the Mark-Houwink-Sakurada equation are also shown in table 1. If the values of λ_∞ obtained from the Dondos Benoit´s equation are compared with the ones from Eq.(5) it can be seen that they are nearly equal, the difference not exceeding 2%. The A values present a similar concordance too. However, it may be observed that the closer the system is to the ideal or theta conditions the better is the concordance between the different parameters.

TABLE 1. Values of λ_∞, A, a and K_θ for the polystyrene(3)/benzene(1)/methanol(2) system.

u_2	λ_∞ ml/g		A		a	$K_\theta \cdot 10^4$
% methanol	Eq.(4)	Eq.(5)	Eq.(4)	Eq.(5)		
10.0	0.127	0.128	2.8	3.3	0.63	8.97
19.0	0.272	0.277	17.6	18.8	0.57	9.12
22.5	0.344	0.348	20.5	20.7	0.53	8.98
25.5	0.412	0.407	25.8	25.6	0.48	8.63

b) Polystyrene(3)/CCl_4(1)/methanol(2). In this system the results obtained for λ_∞ and A with Eqs.(4) and (5) are similar to the ones obtained previously, as shown in Table 2 and Figure 2. In figure 2 both equations for this system at 10% have been represented. The A values are the ones presenting bigger differences between them, due to the fact the Dondos-Benoit´s equation is only useful when the system is found in ideal conditions where

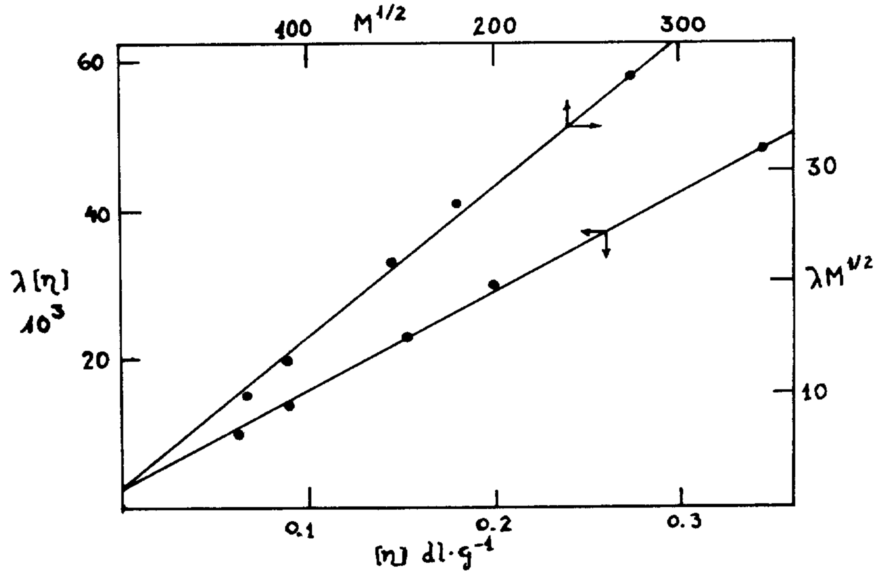

Figure 1. Plots of Eqs.(4) and (5) for polystyrene (3)/benzene(1)/methanol(2) system at u_2 = 10 % methanol.

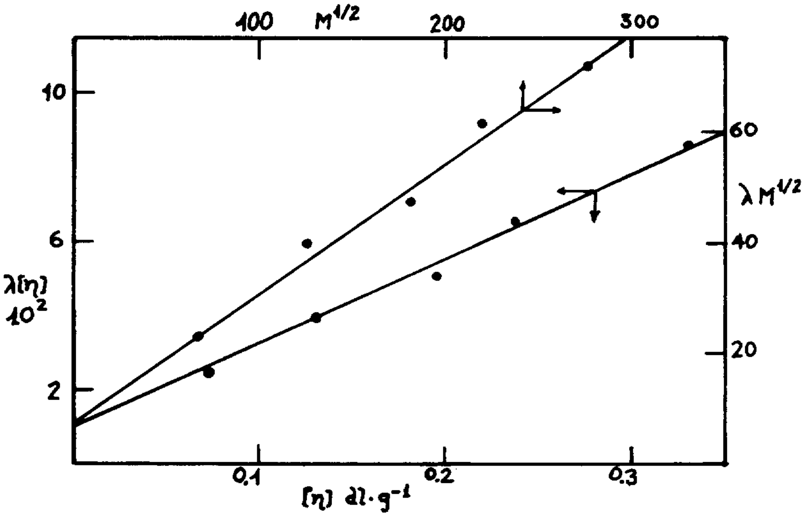

Figure 2. Plots of Eqs.(4) and (5) for polystyrene (3)/CCl_4(1)/methanol(2) system at u_2= 10% methanol.

TABLE 2. Values of λ_∞, A, a and K_θ for the polystyrene(3)/CCl_4(1)/methanol(2) system.

u_2 % methanol	λ_∞ ml/g Eq.(4)	λ_∞ ml/g Eq.(5)	A Eq.(4)	A Eq.(5)	a	$K_\theta \cdot 10^4$ dl/g
10.0	0.187	0.194	15.7	17.9	0.61	8.28
15.0	0.315	0.323	24.7	26.8	0.61	8.92
18.5	0.401	0.404	50.5	51.3	0.51	9.43
21.0	0.488	0.482	28.5	27.8	0.47	9.35
24.0	0.445	0.448	59.3	61.7	0.52	7.85

$\alpha^3 = 1$. Far away from these conditions $\alpha^3 \neq 1$ and the extrapolated A values according to this theory must be always lower than the real ones since α^3 appears in the denominator. This is precisely what is shown in Table 2.

c) Isotactic polybutene(3)/cyclohexane(1)/n-propanol(2). In this case the concordance that has been obtained for both λ_∞ and A is especially good and the differences observed are within experimental error. However, the same considerations that have been done in the previous systems may be also applied here. The fact that at theta composition (u_2 = 30 % n-propanol) both λ_∞ and a are equal is noteworthy. Observing these results it is possible to point out the conclusion that Eqs(4) and (5) are useful when the system is found in ideal conditions;then

TABLE 3. Values of λ_∞, A, a and K_θ for the isotactic polybutene(3)/cyclohexane(1)/n-propanol(2)

u_2 % n-propanol	λ_∞ ml/g Eq.(4)	λ_∞ ml/g Eq.(5)	A Eq.(4)	A Eq.(5)	a	$K_\theta \cdot 10^4$ dl/g
10.0	0.050	0.054	9.6	10.4	0.63	2.73
20.0	0.086	0.092	19.9	20.7	0.59	2.50
30.0	0.132	0.132	33.6	33.6	0.50	2.66
35.0	0.160	0.147	40.0	40.7	0.41	2.75

λ_∞ and A are similar (Table 3). On the other hand, if the system is found far away from the ideality (a >0.5) the Dondos-Benoit´s equation does not lead to the exact values for A, although the λ_∞ ones are very similar to these obtained from Eq.(5)(Figure 3).

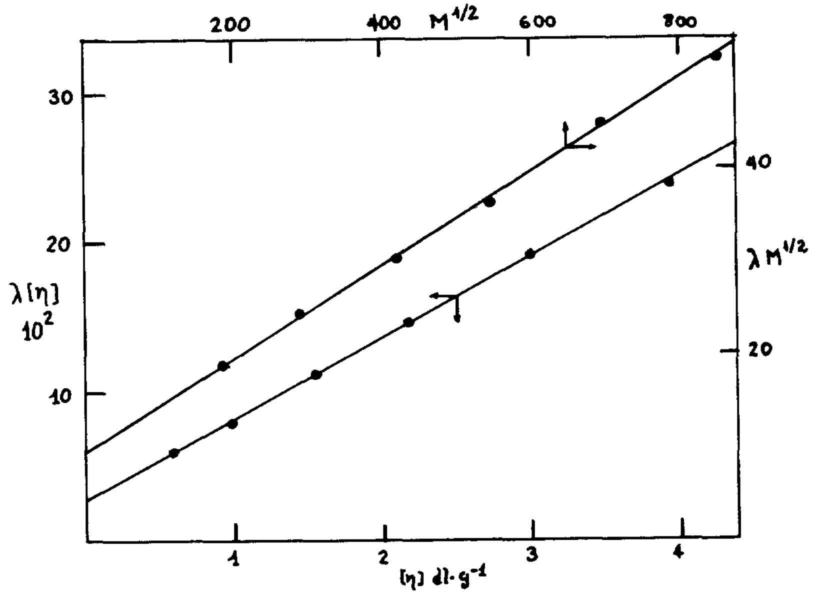

Figure 3. Plots of Eqs.(4) and (5) for isotactic polybutene(3)/cyclohexane(1)/n-propanol(2) system at u_2 = 10 % n-propanol.

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