

Shellac-solvent interaction parameter

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The interaction parameter (μ) of hard and soft segments of shellac with respect to the best alcoholic solvents, i.e., ethyl alcohol and n-butyl alcohol have been estimated using osmotic pressure data. These values of μ have been found to resemble each other closely and are also near to the critical value (μ_c). No segment-segment and no energetic interaction in these solvents takes place, which shows that shellac dissolves molecularly in alcohols without any interaction. The use of this parameter for shellac is indicated in encapsulation.

Keywords Shellac interaction parameter; encapsulation; phase-separation; shellac; shellac-segments; interaction parameter; solubility parameter

The polymer interaction parameter (μ or χ) is a semi-empirical constant which provides a measure of the solvent power of a given liquid for a polymer and plays a valuable role in the quantitative description of properties of polymer solutions. Its values are generally determined by incorporating the appropriate experiments into one or another of the various theoretical equations in which this parameter appears¹⁻⁶. Muthana and Mark⁷ determined μ values of polymers by osmotic pressure measurements and used the following Flory and Huggins¹⁰ equation for the reduced osmotic pressure of dilute polymer solutions.

$$\frac{\pi}{C_2} = A + BC_2$$

or

$$\frac{\pi}{C_2} = \frac{RT}{M_2} + BC_2 \quad (1)$$

Where, $A = \frac{RT}{M_2}$ being an intercept of π/C_2 axis, M_2 is the mol wt of the polymer, and B appears as the slope in the plot of $\frac{\pi}{C_2}$ against C_2 and is given by

$$B = \frac{RT}{V_1 d_2^2} (\frac{1}{2} - \mu) \quad (2)$$

where, π is osmotic pressure, C_2 is concentration of polymer, M_2 is the molecular weight, V_1 is the molar volume of solvent, d_2 is the density of polymer, T is absolute temperature, R is a gas constant and μ is the interaction parameter.

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Shellac is a versatile polyester type of resin formed from fatty and sesquiterpenic acids⁸. It can be broadly separated into hard and soft resin components^{8,9}. Studies on cohesive-energy density of shellac¹⁸ have shown that it is soluble only in moderately and strongly H-bonded solvents and alcohols are the best solvents^{8,9}. With polar solvents there is always a probability of solvent-solute interaction. Basu¹⁰ studied the nature of solvent-solute interaction from osmotic pressure of dilute solutions of hard and soft segments of the lac but did not determine the μ values. The determination of this empirical parameter has, therefore, been done with a view to gaining a better understanding of phase equilibria which is also of use in encapsulation, a rapidly expanding technology.

Values of μ have been calculated from B and other values^{8,10,11} by using equation (2), used by Muthana and Mark⁷. It may be seen that the values of B for hard and soft resin (Table 1) are extremely small and thus the osmotic pressure of the constituents of shellac is nearly proportional to the concentration. The μ of hard and soft components of shellac with respect to ethyl and n-butyl alcohol very closely resemble each other and are very near to critical value ($\mu_c = 0.5$)¹². This suggests that the interaction of the dissolved particles with each other and also the energetic interaction with the solvent are less marked in these cases and the shellac molecules are not solvated in these solutions. This corroborates the earlier observation of Basu¹⁰ and Tanford's¹³ view of ideal polymer solution.

The μ value is known to contain contributions from both entropy and heat of mixing and is also related to the solubility parameter. The $\mu = \mu_s + \mu_h$, where μ_s and μ_h are entropy and heat contributions^{3,17}. The small degree of solvation may lead to larger values of μ_s , thereby increasing the μ value. As per vaan Laar and Hilderband¹¹ the heat of mixing of solvated polymer and

Table 1 Interaction parameter of shellac resin segments

Sl. No.	Shellac resin constituents	M. wt.	Density	Solvents	Molar volume (cc)	δ_s (cal/cc) ^{1/2}	'B' value	μ
1	Hard resin	1900	1.030	(a) Ethyl alcohol	57.5	12.7	0.0074	0.499998
				(b) n-Butyl alcohol	91	11.4	0.0093	0.499958
2	Soft resin	500	1.030	(a) Ethyl alcohol	57.5	12.7	0.0052	0.499998
				(b) n-Butyl alcohol	91	11.4	0.0052	0.499960

solvent should depend on $V_1(\delta_1 - \delta_2)^2$ as $\mu_h = \frac{V_1(\delta_1 - \delta_2)^2}{RT}$

where, δ_1 and δ_2 refer to solvent and solvated polymer and R and T are the gas constant and the absolute temperature respectively^{3,14}. The δ_2 value does not differ very much from solvent to solvent. If these are of the same type, the value δ_1 will determine the magnitude of the endothermic constituent. If δ_1 is sufficiently different from δ_2 , this heat contribution together with μ_s may be large enough to cause μ to exceed its critical value ($\mu_c = 0.5$), which is not evident in case of soft and hard segments of shellac resin. Furthermore the δ_s for both the solvents are near to the δ for the shellac and thus the deviation is small in δ and μ values. The above discussion and μ values of shellac segments indicates that no solvation takes place in both the solvents. As in polymers generally initial phase separation occurs when δ_m (solubility parameters of mixture) differ sufficiently from δ_2 , the value of the polymers to cause μ to exceed its critical value ($\mu_c = 0.5$). Thus this empirical value (μ) of shellac may be used in ascertaining the phase separation in phase separation processes of encapsulation¹⁵⁻¹⁷.

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Letter to Editor

Comments on the kinetic mechanism of free radical bulk copolymerization of styrene-methyl methacrylate*

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The termination mechanism of free radical bulk copolymerization of styrene-methylmethacrylate is chemically controlled as is evident from the literature and the diffusion controlled mechanism postulated by Khan and Wadehra is most likely to be the result of some apparent discrepancies in their experimental data.

Keywords Copolymerization; kinetic mechanism; styrene-methylmethacrylate; ϕ factor; polymerization-bulk; polymerization-free radical

In a recent paper published in this journal¹, Khan and Wadehra attempted to reveal the kinetic mechanism of free radical bulk copolymerization of styrene-methylmethacrylate (SMMA). They showed that the parameter ϕ (which provides a measure of the extent to which termination between unlike radicals is preferred) varies between 127.7 to 20.0 for initiator concentration equal to 0.0076 mol l⁻¹ and from 122.3 to 20.24 for initiator concentration equal to 0.0152 mol l⁻¹, when the mole fraction of styrene decreases from 0.871 to 0.365.

They concluded that the kinetic mechanism in SMMA copolymerization is governed by diffusion controlled termination and is not chemically controlled even when the conversion is limited to a maximum of 7% and the viscosity of the reaction mass is fairly low. It is the purpose of this communication to show that the conclusions arrived by Khan and Wadehra are contrary to the well accepted kinetic mechanism of chemically controlled termination for SMMA copolymerization.

SMMA copolymerization has been well studied in the literature and at least three different groups²⁻⁴ have

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