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Studies on Physico-Chemical Aspects of some Cardopolysulfonates by Densities, Specific Volume and Floation Methods

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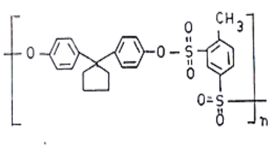
ABSTRACT

The densities of cardopoly sulfonates are determined by specific volume and floatation methods at 300C. The densities determined by floatation method is found in excellent agreement with calculated values but those determined by specific volume (in different solvents) are not in agreement with calculated values in same cases which might be due to apparent change in molecular weights and the intrinsic volumes of repeat units because of solvation phenomena

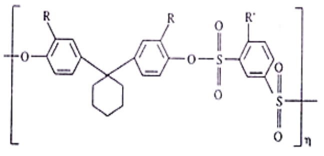
Keywords: Cardopolysulfonates, Density, Packing Coefficient

I. INTRODUCTION

The vast majority of polymers are constituted from a small numbers of different atoms and it is possible to calculate the intrinsic volumes of polymer repeat units from the atomic radii and bond lengths. Slonimskii et al.[1] have reported the volume increments of the various atoms or atomic groups in the repeat unit. They have also reported the intrinsic volumes $\sum \Delta Vi$ and experimental densities of the repeating units of the seventy polymers of widely different structures such as aromatic polyesters, polyamides and polyimides and generalized the packing coefficient as 0.681.



PS-I



PS-2 : R= R^1 = H
PS-3 : R = H and R^1 = CH_3
PS-4 : R = R^1 = CH_3

Barbari et al.[2] have reported the densities of a series of films of polymers based on bis-phenol-A, viz.: polycarbonate, polysulfone. polyarylate. polyether-amide and polyhydroxy ether and also generalized packing coefficient as 0.695.

In the present work authors have determined the densities of bulk and film samples of some cardopolysuifonates PS-1 to PS-4 and attempted to study the effect of solvation on densities.

II. EXPERIMENTAL

All the polysulfonates were synthesized according to our previous Publication[3] and purified prior to use. The solvents such as chloroform (CF), 1,2-dichloroethane (DCE). chlorobenzene (CB), carbontetrachloride (CTC), η-hexane tetrahydrofuran (THF) and 1,4-dioxane (DO) used tor the density measurements were purified by appropriate methods[4] and fractionally distilled prior to use. The densities of the pure solvent and solutions were measured by employing a specific gravity bottle with a precision of $\pm$ 0.0002 g at $30^0 \pm 0.2^0$C

III. RESULTS AND DISCUSSION

Floatation Method[5]

The densities of PS-1 to PS-4 (films) were determined by floatation method using the CTC-□-hexane solvent system at 30°C. The compositions of the two solvents were adjusted in such a way that the film just remained suspended throughout The densities of the mixture were determined after 24 h by the usual method. The average of six measurements alongwith standard deviations is reported in Table-1.

Specific Volume Method[5]

The densities of polymer solutions of different concentrations (0.5-3%) in different solvents were determined by the usual method and fitted to the following Eqn. 1:

$$\frac{1}{W_1\rho_{12}} = \frac{1}{\rho_1} + \frac{W_2}{\rho_2 W_1} \qquad ....(1)$$

The least square densities of PS-1 to PS-4 according to Eqn. 1 are reported in Table 2 alongwith the correlation coefficient (γ).

Table-1 : Densities of PS-1 to PS-4 Determined by Floatation Method Using CCl4-η-Haxane at 300C

Polymer	M	$\sum \Delta V^3$ A	ρ.g cm^{-3} Found	Calcd. (K = 0.695)	% Error
PS-1	470	388.14	1.3530 ± 0.0009	1.3973	-3.1
PS-2	470	388.04	1.3549 ± 0.0003	1.3976	-3.1
PS-3	484	405.24	1.3605 ± 0.0017	1.3782	-1.3
PS-4	512	439.64	1.3183 ± 0.0003	1.3439	-1.9

Table-2 : Densities of PS-1 to PS-4 Determined by Specific Volume Method using Different Solvents at 30^{0}C

Polymer	ρ.g cm^{-3} cald K=06.81	ρ.g cm^{-3} found					Corelation Coeficient, γ				
		CF	DCF	CD	THF	DO	CF	DCE	CB	THF	DO
PS-1	1.3691	1.4615	1.3176	1.4720	1.3617	1.3091	0.9997	0.9993	0.9961	0.9977	0.9997
PS-2	1.3695	1.3675	1.4149	1.3981	1.3162	1.3411	0.9997	0.9984	0.9924	0.9944	0.9989
PS-3	1.3504	1.4363	1.7032	1.2169	1.3523	1.1817	0.9996	0.9864	0.9975	0.9943	1.0005
PS-4	1.3168	1.1469	1.5867	1.2663	-	1.1816	1.0010	0.9872	0.9996	-	0.9977

Table-3 : Solvation Number (Sn) Determined for PS-1 to PS-4 solution (0.5 to 3.0%) from Sound Velocity Measurements in Different Solvents at 30^{0}C

Polymer	Solvation number Sn				
	CF	DCE	CB	THF	DO
PS-1	2.95-3.24	1.38-2.08	3.15-2.06	2.7-4.9	3.49-3.66
PS-2	0.19-0.48	0.35-0.60	0.43-0.61	0.45-0.78	1.2-1.09
PS-3	0.30-0.50	0.51-0.57	0.42-0.68	0.76-0.92	0.91-1.24
PS-4	0.93-1.20	2.00-2.17	2.73-3.27	-	3.48-4.81

Theoretical Calculation of Density

The densities of PS-1 to PS-4 were calculated from the structural aspects[1]:

$$\rho = \frac{KM}{N_A \sum \Delta V_i}$$

where K is the packing coefficient, M is the molecular mass of the polymer repeat unit, $\sum \Delta V_i$ is the intrinsic volume of the polymer repeat unit and N_A is the Avogadro's number. For bulk and film samples the values of K are 0.681 and 0.695. respectively. The calculated values $\sum \Delta V_i$ and ρ are reported in Tables 1 and 2, for film and bulk samples. From Table 1. It is evident that the calculated and experimental densities are in excellent agreement with small relative errors which justified the right choice of K (0.695) for film samples but densities determined in different solvents according to Eqn. 1 (Table 2) are not in agreement with the calculated ones. The disagreement between these values is mainly due to the solvation phenomenon (Table 3) as determined from sound velocity measurements From Table 3, it is evident that the extent of solvation is different in different solvents.

If K is a constant then the density is dependent on M and $\sum \Delta V_i$ (Eqn 2) According to Slonimskii el al.[1] interrmolecular interaction does not have a significant effect on the density of a polymer But the polar substituents brings about a change in volume and in moleculer weight. The discordant values in Table 2 are because of apparent change in M and $\sum \Delta V_i$ as a result of solvation. Thus, according to present authors solvation phenomenon is responsible for the change in M and $\sum \Delta V_i$ and hence ρ. In such circumstances Eqn. 1 is not applicable for the determination of ρ of polymers. Eqn. 1 may be only applicable when solvation is the least The authors suggest the floatation method for the determination of ρ of polymers.

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