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Note

Second virial coefficient and excess thermodynamic functions in benzene of a polymer 2-butene-1,4-diol with adipic acid

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Light scattering measurements of polymer solutions may provide information regarding weight average molecular weight, second virial coefficients, cross linking, polydispersity and mean square radius of gyration etc. The second virial coefficients derived from light scattering measurements and from osmotic pressure measurements have been related to thermodynamic functions[1, 2]. We thought it worthwhile to make light scattering measurements of solutions of 2 butene-1,4-diol with adipic acid at various temperatures in benzene and to calculate the second virial coefficients and excess thermodynamic functions.

EXPERIMENTAL

A polymer sample of 2-butene-1,4-diol with adipic acid was prepared by condensation methods. The sample was characterized by the osmotic vapour pressure method. The number average molecular weight was found to be 900 in carbon tetrachloride. The sample was used without further fractionation. The polymer was purified in benzene. Solvent benzene was purified as described earlier[3].

LIGHT SCATTERING MEASUREMENTS

The glass apparatus and light scattering cells were made dust free by placing these on an acetone fountain. Four solutions with concentrations 4.748×10^{-3}, 7.122×10^{-3}, 9.496×10^{-3} and 11.870×10^{-3} g cm^{-3} were made in benzene from the same polymer sample and from the same batch solutions by dilutions. The solutions were made dust free by centrifuging at a speed of 20,000 r.p.m. for sixty minutes. The solvent benzene was also made dust free by centrifuging at a speed of 15,000 r.p.m. for sixty minutes. Equal volumes of the solutions and solvent were placed in dust free light scattering cells. The light scattering measurements were made with a photo-Gonoi-Diffusiometer (Model No. 42,000) for a vertical polarized radiation of 436 mμ at 283.15, 293.15, 303.15, 313.15, 323.15 and 333.15 K. The temperature was controlled to within 0.1 K. Toluene was used as a bath liquid for light scattering measurements. The intensities were measured at regular intervals of 10° at angles between 20 and 150° using vertically polarized radiation.

Refractive index increments were measured with a differential refractometer at 303.15 K for light of 436 mμ. The temperature was maintained constant to within 0.1 K. The value was found to be 0.0895 cm^3 g^{-1}. This value was used at all other temperatures for calculating the light scattering results.

RESULTS

Ideally the light scattering from a dilute polymer solution may be expressed as

$$Kc/R_\theta = (1/\overline{M}_w)P^{-1}(\theta) + 2\,A_2 \cdot c + 3\,A_3 \cdot c^2 + \ldots \tag{1}$$

where c is the concentration of the sample, $\overline{M}_w$ the weight average molecular weight, A_2 and A_3 the second virial coefficients, R_θ is the excess scattering intensity of the solution over that of the solvent and was determined by comparison with a standard reference (in our case benzene).

The value of the absolute scattering intensity of benzene R_b was taken from the literature[4]. $P^{-1}(\theta)$ is the particle scattering function and K is the optical constant for a particular scattering system and for vertical polarized light is given by

$$K = 4\pi^2\, n_0^2\, (\mathrm{d}n/\mathrm{d}c)^2\, \lambda_0^{-4}\, N^{-1} \tag{2}$$

where n_0 is the refractive index of the solvent, dn/dc is the specific refractive index increment, λ_0 is the wave length of light used in vacuum and N is the Avogadro number.

The refractive index of the solvent was taken from the literature[5]. When the scattering particles are smaller than 1/20th of the wave length of the light used, $P(\theta)$ reduces to unity. Consequently eqn. (1) reduces to

$$\frac{Kc}{R_\theta} = \frac{1}{\overline{M}_w} + 2\,A_2c + 3\,A_3c^2$$

$$= \frac{1}{\overline{M}_w} + \frac{2\,Bc}{RT} + \frac{3\,Cc^2}{RT} \tag{3}$$

where B and C are the osmotic second and third virial coefficient. All other symbols in eqns. (1) and (2) have the same significance as given elsewhere[6].

DISCUSSION

Kc/R_θ is a function of concentration c and also of angle θ. It is necessary to plot Kc/R_θ against concentration c and against angle θ. Zimm[7] has given a method for plotting Kc/R_θ against concentration and angle in one plot. A double extrapolation procedure is employed plotting Kc/R_θ against $h^2 + kc$ and extrapolating at constant

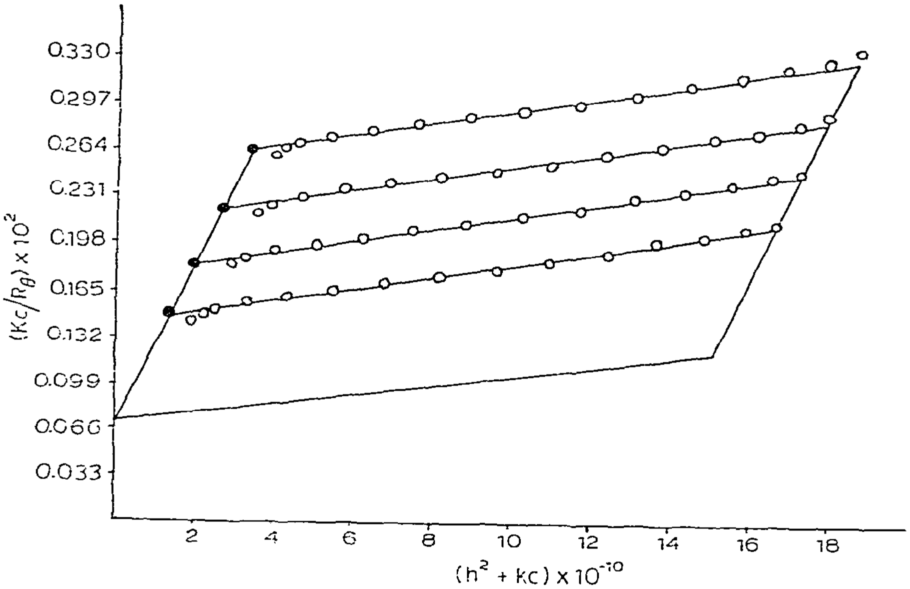

Fig. 1. Plot of $Kc/R\theta$ against $h^2 + kc$ for 2-butene-1,4-diol with adipic acid at 283.15 K.

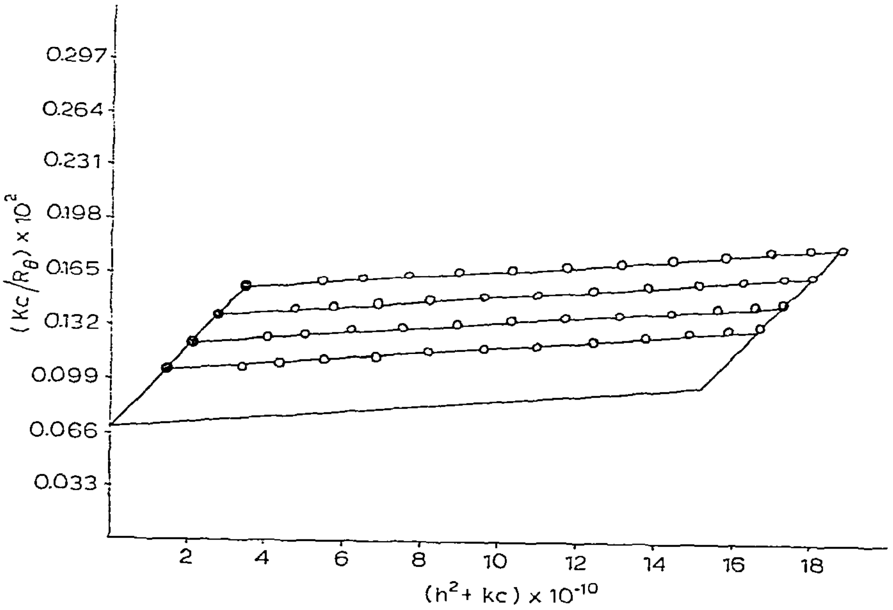

Fig. 2. Plot of $Kc/R\theta$ against $h^2 + kc$ for 2-butene-1,4-diol with adipic acid at 333.15 K.

concentration and constant angle to give a grid. Here k is an adjustable constant and is given by

$$h = \frac{(4\pi n \sin \theta/2)}{\lambda_0} \tag{4}$$

where λ_0 is the wave length of the light in vacuum and n is approximated to n_0. The value of k in our plots is 0.3×10^{13}. A double extrapolation is made to zero

TABLE 1

SECOND VIRIAL COEFFICIENTS AND EXCESS THERMODYNAMIC FUNCTIONS OF 2-BUTENE-1,4-DIOL WITH ADIPIC ACID IN BENZENE

Temperature (K)	$B = -\Delta\mu_1^E/(c^2v_1)$ *(J cm³ g⁻²)*		$B' = dB/dT$ *(J cm g⁻² deg⁻¹)*	$\Delta h_1^E/(c^2v_1)$ *(J cm³ g⁻²)*	$T\Delta S_1^E/(c^2v_1)$ *(J cm³ g⁻²)*
	Exptl.	*Interpol.*			
283.15	80.0				
288.15		97.3	3.45	896.8	994.1
293.15	114.5				
298.15		131.6	3.41	885.1	1016.7
303.15	148.7				
308.15		165.5	3.33	860.6	1026.1
313.15	182.2				
318.15		198.6	3.27	841.8	1040.3
323.15	214.9				
328.15		230.7	3.16	806.3	1037.0
333.15	246.5				

angle and zero concentration so as to cut the Kc/R_θ axis at the same point. The light scattering results were found to be correct within 1 %.

The plots of Kc/R_θ against $h^2 + kc$ have been made at 283.15, 293.15, 303.15, 313.15, 323.15 and 333.15 K. In this paper the plots at 283.15 and 333.15 K are only shown in Figs. 1 and 2.

From the slope of the Zimm plot we get

$$\lim_{c\to 0} \mathrm{d}\left(\lim_{\theta\to 0} \frac{Kc}{R_\theta}\right)\Big/\mathrm{d}c = 2A_2 = \frac{2B}{RT} \tag{5}$$

The second virial coefficients have been calculated from the slopes and are recorded in Table 1.

Reik and Gebert[1] have derived relations between osmotic second virial coefficients and excess thermodynamic functions. Cantow[2] has related second and third virial coefficients to the excess thermodynamic functions. The relations are given by

$$\frac{\Delta\mu_1^E}{c^2v_1} = -B - Cc \tag{6}$$

$$\frac{\Delta h_1^E}{c^2v_1} = -B'T - B + C'Tc - Cc \tag{7}$$

$$\frac{T\Delta S_1^E}{c^2v_1} = B'T + C'cT \tag{8}$$

where $\Delta\mu_1^E$, Δh_1^E and ΔS_1^E are the excess free energy, excess enthalpy and excess entropy, c is the concentration of the sample, v_1 the molar volume, B' and C' are the temperature coefficients of the second and third virial coefficients i.e. $B' = \mathrm{d}B/\mathrm{d}T$ and $C' = \mathrm{d}C/\mathrm{d}T$.

Excess thermodynamic functions were calculated for the second virial coefficients and from their temperature coefficients. The effect of third virial coefficients was not considered. The functions $\Delta\mu_1^E/(c^2v_1)$, $\Delta h_1^E/(c^2v_1)$ and $T\Delta S_1^E/(c^2v_1)$ are recorded in Table 1.

From Table 1 it is clear that second virial coefficients are positive at all temperatures but do not become zero at 283.15 K. The solution does not become ideal in this temperature range. The enthalpy and entropy terms compete well with each other. The entropy terms multiplied by temperature are larger than the enthalpy terms, making the free energy negative. The θ-temperature for this polymer sample–solvent system is not reached in the temperature range studied.

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