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SECOND VIRIAL COEFFICIENTS OF A POLYMER OF 2-BUTENE-2,3-DIBROMO-1,4-DIOL WITH ADIPIC ACID FROM LIGHT SCATTERING MEASUREMENTS IN BENZENE

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ABSTRACT

Light scattering measurements of a polymer of 2-butene-2,3-dibromo-1,4-diol with adipic acid in benzene have been made in the temperature range 283.15–333.15 K. The second virial coefficients and excess thermodynamic functions have been calculated.

INTRODUCTION

Light scattering measurements of solutions may provide information regarding the second virial coefficients. Many workers[1–15] successfully formulated the thermodynamic theory of polymer solutions and recently[16–20], workers have correlated the light scattering results with the thermodynamic theory of polymer solutions. The second virial coefficients obtained from light scattering measurements may be used to obtain excess thermodynamic functions.

EXPERIMENTAL

Benzene was purified as described earlier[21]. The polymer sample was prepared by condensation methods. It was found to be a sharp fraction, was used without further fractionation and was purified from benzene.

Light scattering measurements

The light scattering cells and other glass apparatus was made dust free by placing them on an acetone fountain. Four solutions of 4.748, 7.122, 9.496 and 11.870 g l^{-1} of the sample in benzene were prepared from the same sample from one batch solution by dilution. The solutions were made dust free by centrifugation at a speed of 15,000 r.p.m. for 60 min. Equal volumes of the dust free solutions were transferred to light scattering cells. Light scattering measurements for a vertical polarized light of 436 mμ were made in the temperature range 283.15–333.15 K with a Photo-Gonio-Diffusiometer (Model No. 42.000). The measurements were made at a regular intervals of 10° between angles of 30 and 150°. The temperature in the light scattering bath was controlled to within 0.1 K. Toluene was used as bath liquid and benzene as a reference standard.

Refractive index increments were measured in benzene with a differential refractometer with a light of 436 mμ at 303.15 K. The value was found to be 0.0896 ml g^{-1} and this value was used at all other temperatures for calculating the light scattering parameters.

RESULTS AND DISCUSSION

Light scattering from a dilute polymer solution may be expressed as

$$\frac{Kc}{R_\theta} = \frac{1}{\overline{M}_w P^{-1}(\theta)} + 2A_2c + 3A_3c^2 + \ldots \tag{1}$$

where $\overline{M}_w$ is the weight average molecular weight and A_2 and A_3 are the second and third virial coefficients. 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 and N is the Avogadro number. The refractive index of the solvent was taken from the literature[22].

R_θ in eqn. (1) is the measured excess scattering intensity of the solution over that of the solvent. It was determined by comparison with a standard reference substance, in this case with benzene. The value of the absolute scattered intensity of benzene, R_b, was taken from the literature[23]. The values of R_θ are then calculated from

$$\frac{R_\theta}{R_b} = \frac{i_\theta}{i_b} \tag{3}$$

where i_θ and i_b are the measured potentiometric readings for the solution and benzene at a particular angle θ.

The term $P(\theta)$ in eqn. (1) describes the angular variation of light scattered at constant concentration. When the scattering particles are less than 1/20th of the wavelength of the light used, the contributions to $P(\theta)$ caused by destructive interference of light become negligible and $P(\theta)$ reduces to unity. Consequently, eqn. (1) becomes

$$\begin{aligned}\frac{Kc}{R_\theta} &= \frac{1}{\overline{M}_w} + 2A_2c + 3A_3c^2 + \ldots \\ &= \frac{1}{\overline{M}_w} + \frac{2Bc}{RT} + \frac{3Cc^2}{RT} + \ldots \end{aligned} \tag{4}$$

where B and C are osmotic second and third virial coefficients. All other symbols in eqns. (1) and (2) have the same significance as described elsewhere[24].

Since Kc/R_θ is a function of concentration and angle θ, it becomes necessary to have double plot of Kc/R_θ against concentration and angle. The Zimm[25] treatment affords a most accurate graphical procedure for the derivation of light scattering parameters. A double extrapolating procedure is employed plotting Kc/R_θ against $(h^2 + kc)$ and extrapolating at constant concentration and constant angle to give a grid. In this method, k is an adjustable constant and h is given by

$$h = \frac{4\pi n \sin(\theta/2)}{\lambda_0} \tag{5}$$

where λ_0 is the wavelength of the light in vacuum and n is approximated to n_0.

The value of k in our plots is 0.3×10^{13}. The Zimm plots of Kc/R_θ against $(h^2 + kc)$ were made at 283.15, 293.15, 303.15, 313.15, 323.15 and 333.15 K in Figs. 1 to 6, respectively.

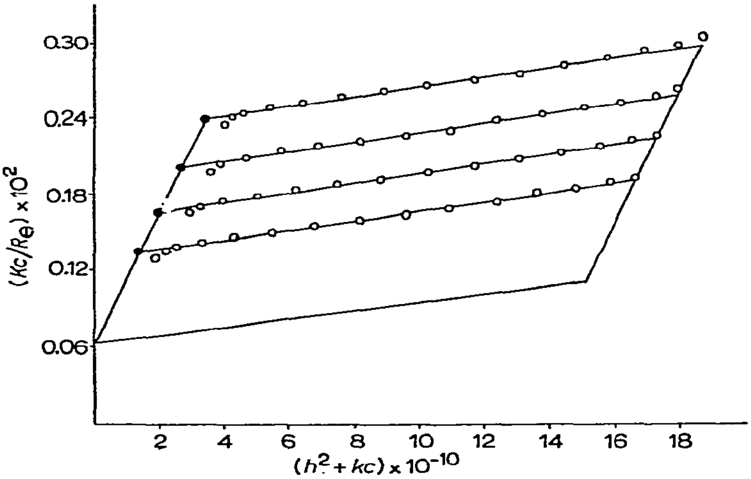

Fig. 1. Plot of Kc/R_θ against $(h^2 + kc)$ for 2-butene-2,3-dibromo-1,4-diol with adipic acid at 283.15 K.

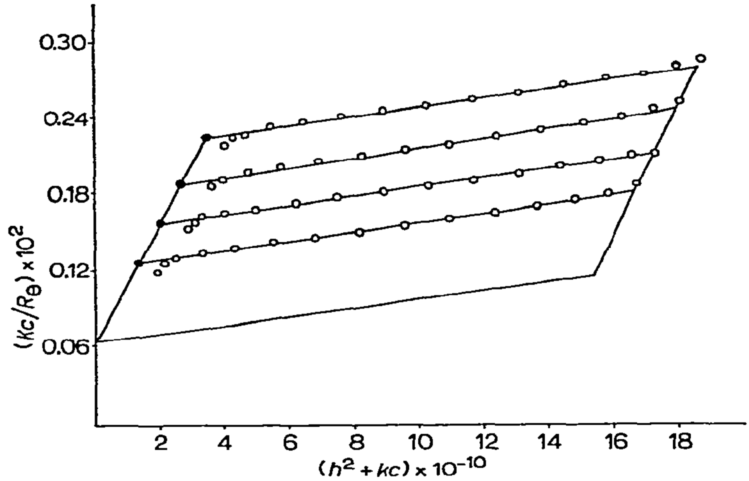

Fig. 2. Plot of Kc/R_θ against $(h^2 + kc)$ for 2-butene-2,3-dibromo-1,4-diol with adipic acid at 293.15 K.

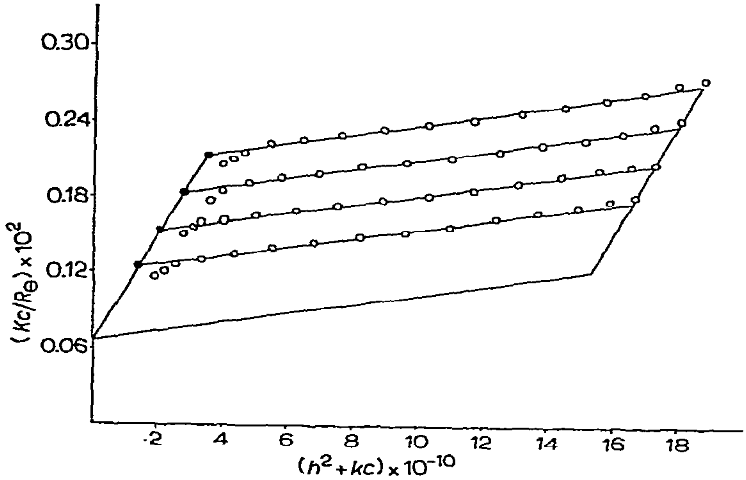

Fig. 3. Plot of Kc/R_θ against $(h^2 + kc)$ for 2-butene-2,3-dibromo-1,4-diol with adipic acid at 303.15 K.

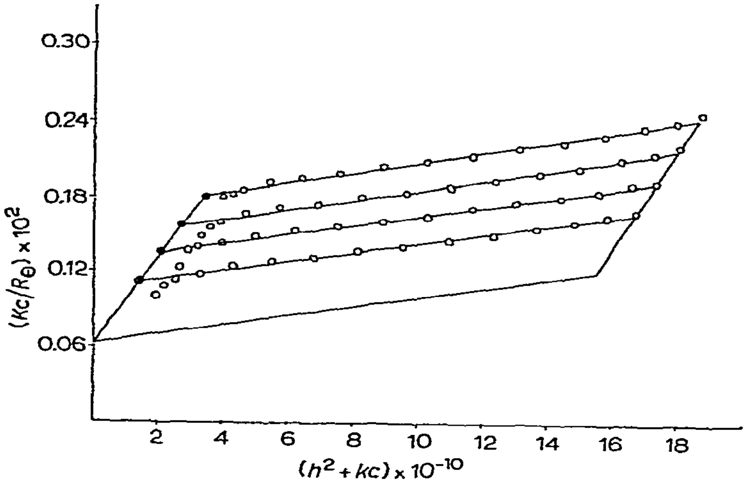

Fig. 4. Plot of Kc/R_θ against $(h^2 + kc)$ for 2-butene-2,3-dibromo-1,4-diol with adipic acid at 313.15 K.

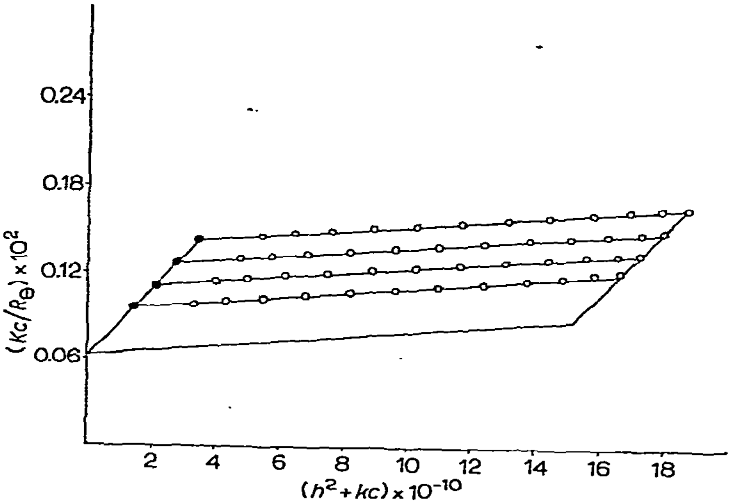

Fig. 5. Plot of Kc/R_θ against $(h^2 + kc)$ for 2-butene-2,3-dibromo-1,4-diol with adipic acid at 323.15 K

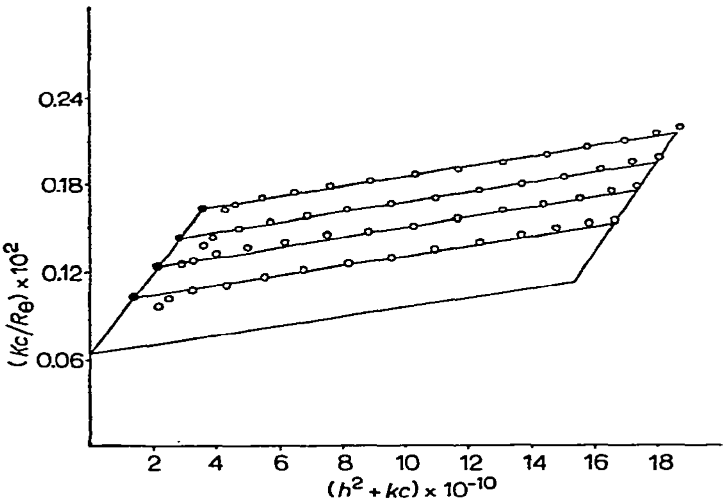

Fig. 6. Plot of Kc/R_θ against $(h^2 + kc)$ for 2-butene-2,3-dibromo-1,4-diol with adipic acid at 333.15 K.

TABLE 1

SECOND VIRIAL COEFFICIENTS AND EXCESS THERMODYNAMIC FUNCTIONS

Temperature	$B = -\Delta\mu_1{}^E/c^2v_1{}^*$ *(J.cm³ g⁻²)*	$B' = dB/dT^{**}$ *(J cm³ g⁻² deg⁻¹)*		$B'T = T\Delta S_1{}^E/c^2v_1{}^{**}$ *(J.cm³ g⁻²)*	$B'TB = \Delta h_1{}^E/c^2v_1{}^{**}$ *(J.cm³ g⁻²)*
283.15	70.6				
288.15		85.3	2.93	844.3	758.9
293.15	99.9				
298.15		114.2	2.86	852.7	738.5
303.15	128.5	142.4	2.78		
308.15		142.4	2.78	856.7	714.3
313.15	156.2				
318.15		169.4	2.65	843.1	673.7
232.15	182.7				
328.15		195.2	2.50	820.4	625.2
333.15	207.7				

* Experimental results.
** Intrapolated results.

The lines were extrapolated to zero concentration and zero angle to cut the Kc/R_θ axis at the same point. From the slope we get

$$\lim_{c\to0} \mathrm{d}\,(\lim_{\theta\to0} Kc/R_\theta)/\mathrm{d}c = 2A_2 = 2B/RT \qquad (6)$$

The second virial coefficients were determined from the slopes at all the temperatures and are recorded in Table 1.

The excess free energy $\Delta\mu_1^E$, excess enthalpy Δh_1^E and excess entropy ΔS_1^E are given by[15, 20]

$$\Delta\mu_1^E = -Bc^2v_1 - Cc^3v_1 \qquad (7)$$

$$\Delta h_1^E = (B'T - B + C'cT - Cc)c^2 v_1 \tag{8}$$

$$\Delta S_1^E = (B' + C'c)c^2 v_1 \tag{9}$$

From eqns. (7)–(9), we can write up to the second virial coefficients

$$\Delta \mu_1^E / c^2 v_1 = - B \tag{10}$$

$$\Delta h_1^E / c^2 v_1 = B'T - B \tag{11}$$

$$T \Delta S_1^E / c^2 v_1 = B'T \tag{12}$$

In these equations, c is the concentration of the sample, v_1 is the molar volume of the solvent, B' is the temperature coefficient of the second virial coefficient and T is the temperature.

The excess thermodynamic functions $\Delta\mu_1^E/c^2v_1$, $\Delta h_1^E/c^2v_1$ and $T\,\Delta S_1^E/c^2v_1$ were calculated from the second virial coefficients and from their temperature coefficients and are recorded in Table 1. The thermodynamic parameters are plotted against temperature in Fig. 7.

From Table 1 and Fig. 7, it is clear that the excess free energy $\Delta\mu_1^E$ is negative, and the excess enthalpy and excess entropy are positive. The excess free energies increase with decrease in temperature. The second virial coefficients are positive in the temperature range 283.15–333.15 K and decrease with decrease in temperature. The second virial coefficients and excess free energy do not become zero even at 283.15 K, indicating that the θ-temperature for this polymer–solvent system is not reached. The system does not become ideal in the temperature range studied. The temperature coefficient of the second virial coefficient decreases with increasing temperature. The

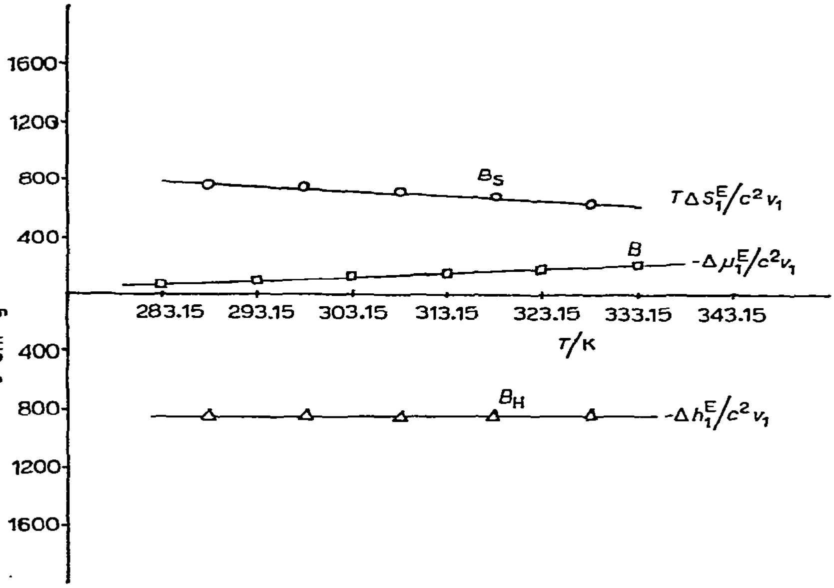

Fig. 7. Plot of $-\Delta\mu_1^E/c^2v_1$, $-\Delta h_1^E/c^2v_1$ and $T\,\Delta S_1^E/c^2v_1$ against temperature, T.

excess entropy function first increases and then decreases slightly with temperature. The excess enthalpy function decreases with increase in temperature. The plots of the second virial coefficient B, entropy function

$$B'T = T\Delta S_1^E/c^2v_1$$

and enthalpy function

$$B'T - B = \Delta h_1^E/c^2v_1$$

against temperature T K are linear. The enthalpy and entropy terms compete well with each other.

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