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SECOND VIRIAL COEFFICIENTS AND EXCESS THERMODYNAMIC FUNCTIONS OF 2-BUTENE-1,4-DIOL WITH SUCCINIC ACID IN BENZENE FROM LIGHT SCATTERING MEASUREMENTS

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ABSTRACT

Light scattering measurements on 2-outene-1,4-diol with succinic acid have been made in benzene in the temperature range 283.15–333.15 K. The second virial coefficients and excess thermodynamic functions of the sample in benzene have been calculated from light scattering results.

INTRODUCTION

Measurements of the light scattering of polymer solutions may provide information regarding weight-average molecular weight, second virial coefficients, mean square radius of gyration, form factor and polydispersity, etc. In recent years, many workers[1-15] have developed the thermodynamic theory of polymer solutions. More recently[16-20] the light scattering results have been correlated with the thermodynamic functions of the solutions. We thought it worthwhile to make light scattering measurements on 2-butene-1,4-diol with succinic acid in benzene, and to derive the second virial coefficients and also the thermodynamic functions from the light scattering results.

EXPERIMENTAL

Benzene was purified as described earlier[21]. The sample 2-butene-1,4-diol with succinic acid was purified from benzene.

Light scattering measurement. The light scattering cells and other glass apparatus were made dust free by placing them on an acetone fountain. Four solutions, of concentrations 4.748, 7.122, 9.496 and 11.870 gl^{-1}, were prepared in benzene. The solutions were made dust free by centrifugation at a speed of 20,000 r.p.m. for about sixty minutes. The solvent benzene was also made dust free by centrifugation at a speed of 15,000 r.p.m. for about sixty minutes. Equal volumes of dust-free solutions and solvent were taken into dust-free light scattering cells. The light scattering measurements for vertically-polarized radiation of 436 $m\mu$ were made using a Photo-Gonio-Diffusiometer (Model No. 42.000) at 283.15, 293.15, 303.15, 313.15, 323.15

and 333.15 K. The temperature in the light scattering bath was controlled to within 0.1 K. The measurements were made at regular angular intervals of 10° in the range 20–150°. Toluene was used as the bath liquid for light scattering measurements.

Refractive index increments were measured in benzene using a differential refractometer with radiation of 436 mμ at 303.15 K, and the value was found to be 0.0866 ml g^{-1}. This value was used at all other temperatures for calculating the light scattering parameters.

RESULTS

The light scattering from a dilute polymer solution may be expressed as:

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

where $\bar{M}_w$ 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, and $\mathrm{d}n/\mathrm{d}c$ is the specific refractive index increment. 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 pure solvent. R_θ was determined by comparison with a standard reference: the reference substance in the present work was benzene. The value of absolute scattered intensity of benzene, R_b, was taken from the literature[23]. The values of R_θ are then calculated in the following manner:

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

where i_θ and i_b are the measured voltmeter readings for the solution and benzene, respectively, at a particular angle θ. The calculated light scattering results are found to be correct to within 1%.

The term $P(\theta)$ in eqn. (1) describes the angular variation of light scattered at constant concentration. The form of $P^{-1}(\theta)$ is dependent on the size and shape of the scattering particle. When the scattering particles are smaller than 1/20th of the wavelength of the light used, the contributions to $P(\theta)$ caused by destructive interference of light becomes negligible and $P(\theta)$ reduced to unity. Consequently, eqn. (1) becomes

$$Kc/R_\theta = 1/\bar{M}_w + 2A_2 \cdot c + 3A_3 \cdot c^2 + \dots$$

$$= 1/\bar{M}_w + 2B \cdot c/RT + 3C \cdot c^2/RT + \dots \tag{4}$$

All other symbols in eqns. (1), (2) and (3) have the same significance as in ref. 24.

DISCUSSION

Kc/R_θ is a function of concentration c and of angle θ. It is therefore necessary to make a double plot of Kc/R_θ, against concentration c and against angle θ. Zimm[25] has given a method for plotting Kc/R_θ against concentration c and against angle θ in the same plot for both. The Zimm treatment affords the most accurate graphical procedure for the derivation of light scattering parameters. A double extrapolation procedure is employed, plotting Kc/R_θ against $h^2 \div kc$ and extrapolating at constant

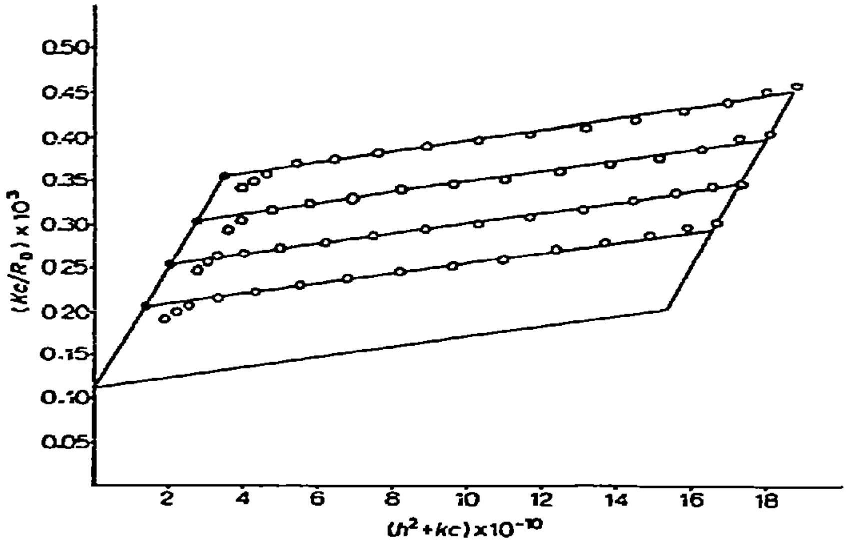

Fig. 1. Plot of Kc/R_θ against $h^2 \div kc$ for 2-butene-1,4-diol with succinic acid at 283.15 K. In Figs. 1–6, experimental points are denoted by ○○○, and extrapolations to zero angle by ●●●.

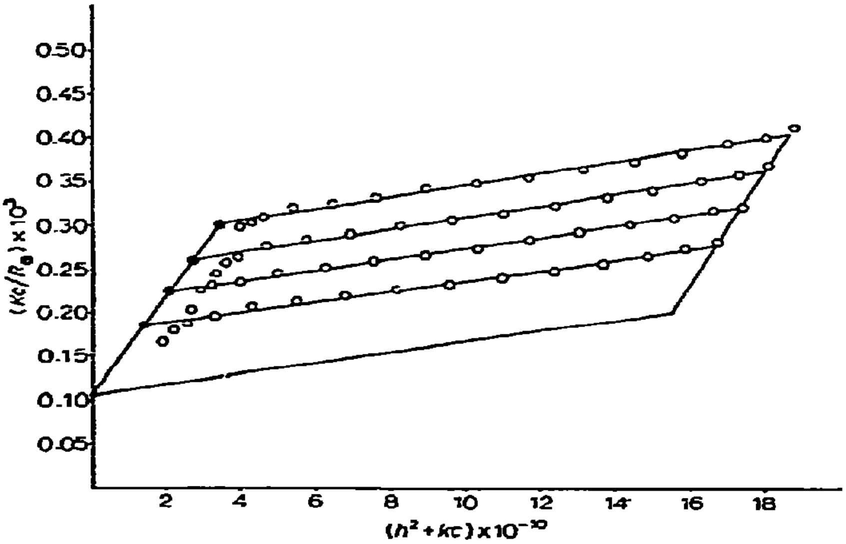

Fig. 2. Plot of Kc/R_θ against $h^2 \div kc$ for 2-butene-1,4-diol with succinic acid at 293.15 K.

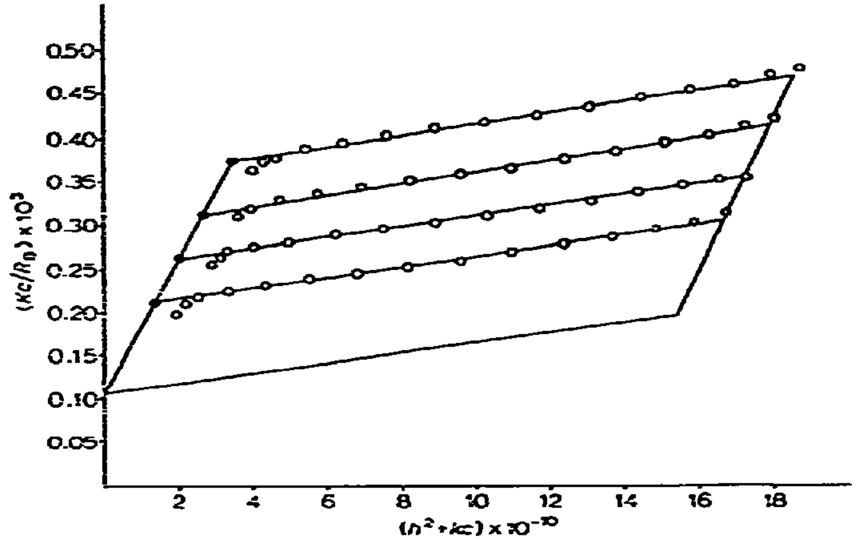

Fig. 3. Plot of Kc/R_θ against $h^2 + kc$ for 2-butene-1,4-diol with succinic acid at 303.15 K.

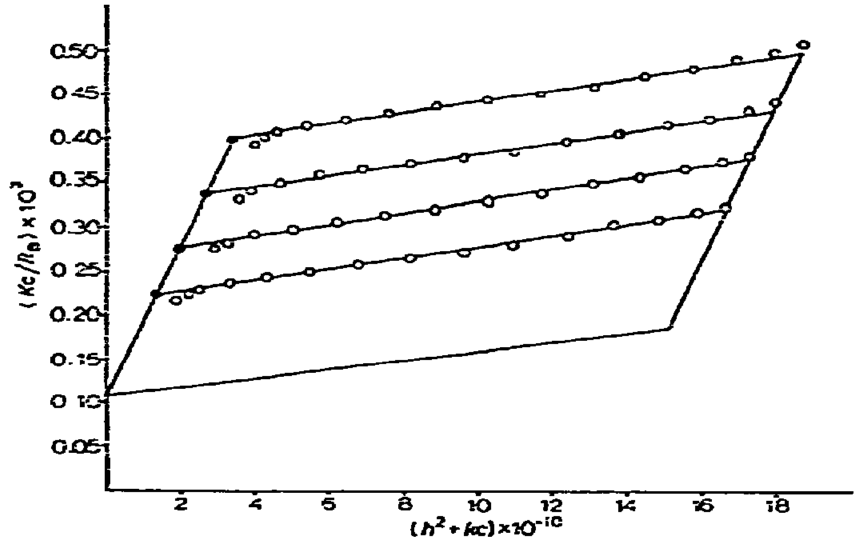

Fig. 4. Plot of Kc/R_θ against $h^2 + kc$ for 2-butene-1,4-diol with succinic acid at 313.15 K.

concentration and constant angle to give a grid. In this method, k is an adjustable constant (in the present work, $k = 0.3 \times 10^{13}$). The parameter h is given by

$$h = [4\pi n \sin(\theta/2)]/\lambda_0 \qquad (5)$$

The Zimm plots of Kc/R_θ against $h^2 + kc$ at 283.15, 293.15, 303.15, 313.15, 323.15 and 333.15 K are shown in Figs. 1–6. The lines in the Figures were extrapolated to zero concentration and zero angle to cut the Kc/R_θ axis at the same point.

From the slope we obtain

$$\lim_{c \to 0} \mathrm{d}(\lim_{\theta \to 0} Kc/R_\theta)/\mathrm{d}c = 2A_2 = 2B/RT \qquad (6)$$

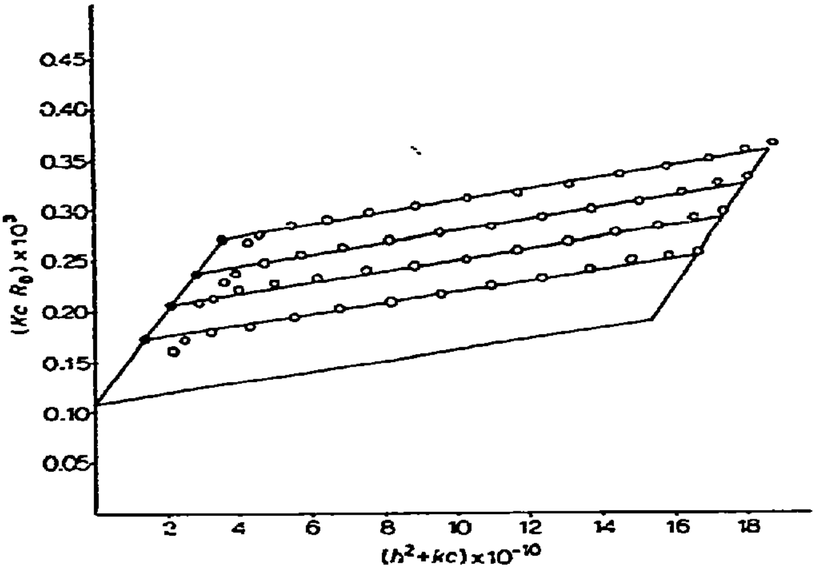

Fig. 5. Plot of Kc/R_θ against $h^2 + kc$ for 2-butene-1,4-diol with succinic acid at 323.15 K.

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

TABLE 1

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

Temperature (K)	$B = -\Delta\mu_1^E/c^2\cdot v^1$ *(J cm³ g⁻²)*		*B′ (J cm³ g⁻² deg⁻¹)*	$\Delta h_1^E/c^2\cdot v_1$ *(J cm³ g⁻²)*	$T\Delta S_1^E/c^2\cdot v_1$ *(J cm³ g⁻²)*
	Exp.	*Extrapol.*			
283.15	11.03				
288.15		13.68	0.530	139.0	152.7
293.15	16.33				
298.15		18.88	0.509	132.8	151.7
303.15	21.42				
308.15		23.73	0.461	118.3	142.1
313.15	26.03				
318.15		28.15	0.423	106.5	134.6
323.15	30.23				
328.15		32.30	0.408	101.6	133.9
333.15	34.34				

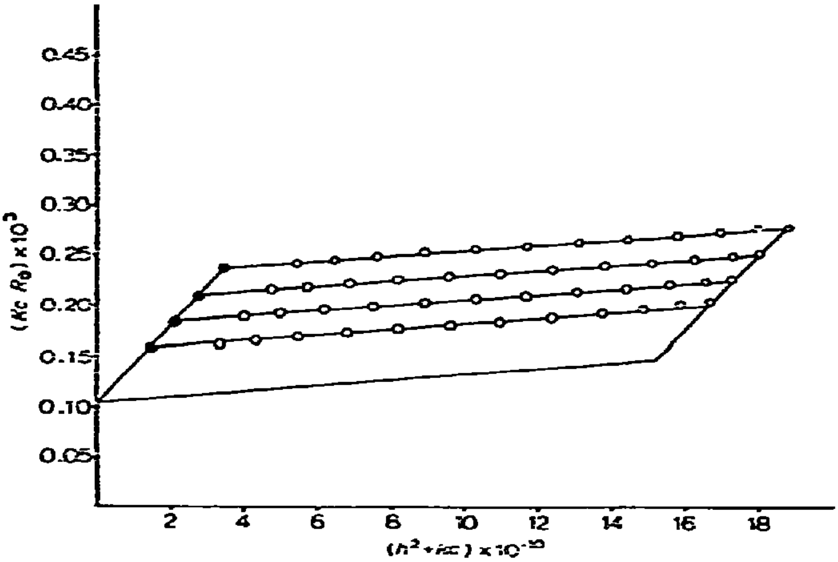

Fig. 6. Plot of Kc/R_θ against $h^2 + kc$ for 2-butene-1,4-diol with succinic acid at 333.15 K.

THERMODYNAMIC FUNCTIONS FROM LIGHT SCATTERING

The osmotic pressure π may be related[26] to the chemical potential difference of the solution $(\mu_1 - \mu_1^0)$ by the equation

$$\pi = -(\mu_1 - \mu_1^0)/v_1 = -\Delta\mu_1/v_1 \tag{7}$$

where v_1 is the molar volume of the solvent. The osmotic pressure is related to the second and third coefficients as follows:

$$\pi/c = RT/M + B.c + C.c^2 + \ldots \tag{8}$$

where c is the concentration of the sample.
From eqns. (7) and (8) we obtain

$$\Delta\mu_1 = -\left[(RT/M).c + B.c^2 + C.c^3 + \ldots\right)v_1 \tag{9}$$

The enthalpy difference Δh_1 and entropy difference ΔS_1 are given by the equations

$$\Delta h_1 = -\left[\partial(\Delta\mu_1/T)/\partial T\right]\cdot T^2$$

$$= (B'.T - B + C'.c.T - C.c)c^2.v_1 \tag{10}$$

and

$$\Delta S_1 = -\partial(\Delta\mu_1)/\partial T$$

$$= (R.c/M + B'.c^2 + C'.c^3)v_1 \tag{11}$$

where B' $(= dB/dT)$ and C' $(= dC/dT)$ are the temperature coefficients of the second and third virial coefficients, respectively. The solution becomes ideal when the contributions to the thermodynamic functions from 2nd and 3rd virial coefficients, and also from their temperature coefficients, vanish.

Ideal free energy, $\Delta\mu_1^*$, ideal enthalpy Δh_1^* and ideal entropy ΔS_1^* are given by

$$\Delta\mu_1^* = -RT.c.v_1/M \tag{12}$$

$$\Delta h_1^* = 0 \tag{13}$$

$$\Delta S_1^* = R.c.v_1/M \tag{14}$$

The excess free energy $\Delta\mu_1^E$, excess enthalpy Δh_1^E and excess entropy ΔS_1^E are then given by

$$\Delta\mu_1^E = \Delta\mu_1 - \Delta\mu_1^* = -B.c^2.v_1 - C.c^3.v_1 \tag{15}$$

$$\Delta h_1^E = \Delta h_1 - \Delta h_1^* = (B'.T - B + C'.c.T - C.c)c^2.v_1 \tag{16}$$

$$\Delta S_1^E = \Delta S_1 - \Delta S_1^* = (B' + C'.c)c^2.v_1 \tag{17}$$

From eqns. (15), (16) and (17) we can write

$$\Delta\mu_1^E/c^2.v_1 = -B - C.c \tag{18}$$

$$\Delta h_1^E/c^2.v_1 = B'.T - B + C'.c.T - C.c \tag{19}$$

$$T\Delta S_1^E/c^2.v_1 = B'.T + C'.c.T \tag{20}$$

The second virial coefficients were calculated from the slope of Zimm plots. The excess functions $\Delta\mu_1^E/c^2 \cdot v_1$, $\Delta h_1^E/c^2 \cdot v_1$ and $T\Delta S_1^E/c^2 \cdot v_1$ were calculated from the

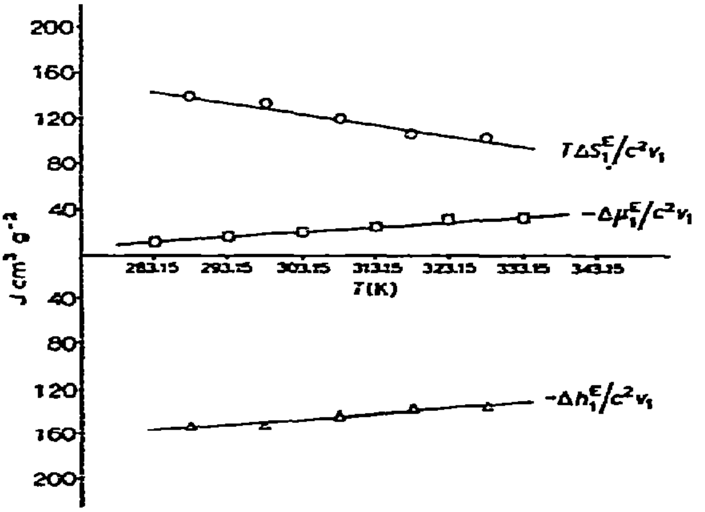

Fig. 7. Plot of $-\Delta\mu_1{}^E/c^2v_1$, $-\Delta h_1{}^E/c^2v_1$ and $T\Delta S_1{}^E/c^2v_1$ against temperature T.

second virial coefficients and their temperature coefficients. The influences of third virial coefficients were not considered significant. The thermodynamic excess functions are recorded in Table 1 and are plotted in Fig. 7.

It is evident from Table 1 and Fig. 7 that the second virial coefficients are positive at all temperatures in the range 283.15–333.15 K. The second virial coefficients decrease with decreasing temperature but do not become zero. The solution does not become ideal in this temperature range. The excess free energies are negative and increase with decreasing temperature. The enthalpy and excess entropy functions are positive and these decrease with increasing temperature. The excess enthalpy and excess entropy terms are competing with each other. The excess entropy terms multiplied by temperature are larger than the excess enthalpy terms at all stages.

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