

# Correlation between the combinatorial entropy of polymer and ideal liquid solutions: 3. Derivation of equation for local concentration

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The local concentration in binary solutions of polymer in solvent and in simple liquid solution has been determined by an equation derived from the maximum condition of the number of configurations in the binary solution with two hypothetical regions, a small region and the rest. The equation for a solution of flexible polymer with  $r$  segments in solvent is given by:

$$\ln(\phi_1^2 X_2 / X_1^2 \phi_2) + \{k - (1 - k)/r\} \ln(\phi_2 / X_2) + k(1 - r^{-1})(\phi_2 - X_2) + k \ln(N_i^* / n_i^*) = 0$$

where  $X_i$  is the local volume fraction of polymer ( $i=2$ ) and solvent ( $i=1$ ),  $\phi_i$  is the mean or macroscopic volume fraction,  $k$  is a parameter defined by  $k = \pm \{1 + (V_2^0 / V_1^0)(\partial n_2 / \partial n_1)_v\}$  and  $V_i^0$  is the molar volume of  $i$  and  $n_i$  is the number of molecules of  $i$  in the small region,  $n_i^* = n_i + r n_2$ , and  $N_i^*$  is the total number of molecules in the solution. It is found that the maximum concentration fluctuation in the small region around the mean concentration  $\phi_1$  characterized by  $|X_1 - \phi_1|$  is proportional to  $|k|$  and is zero for  $k=0$ .

(Keywords: combinatorial entropy; ideal liquid solution; local concentration)

## INTRODUCTION

Investigations on a local or microscopic concentration in polymer solution and its relation to the mean or macroscopic concentration and of a local concentration fluctuation are very important in understanding the thermodynamic properties of polymer solution. Wilson<sup>1</sup> proposed a concept of local concentration, such as a local volume fraction, which depends on an interaction energy between solvent and solute and is not equal to the macroscopic volume fraction generally. The concept of local concentration or non-randomness in solution has been applied to polymer solutions and discussed by Abrams and Prausnitz<sup>2</sup>, Renuncio and Prausnitz<sup>3</sup>, Brandani<sup>4</sup> and Rubio and Renuncio<sup>5</sup>. A correlation between the interacting surface fraction and volume fraction has been discussed by Koningsveld and Kleintjens<sup>6</sup> in evaluating the pair-interaction parameter corresponding to the  $\chi$  parameter in the Flory-Huggins theory<sup>6</sup>. On the other hand, there have been theoretical approaches to the local concentration or non-random mixing. Fixman<sup>7</sup> has derived the thermodynamic theory of polymer solution which covers the entire concentration range from dilute to concentrated solution and shows that at low concentration the result is identical to that in imperfect gas theory and the random mixing model is found to hold at high concentration. The theory of composition fluctuation in solution has been derived by Kirkwood and Buff<sup>8</sup> based on the statistical mechanics theory. The Kirkwood-Buff theory has been applied to polymer solution and a reasonable prediction is obtained over non-critical and critical regions<sup>9,10</sup>.

The random mixing model is unquestionably the

simplest approximation for the concentration or solution structure in solution and the model shows that the local concentration is equal to that determined macroscopically and therefore the solution is completely uniform in the range  $10^{-30}$ – $10^{-6}$  m<sup>3</sup>, for example. It is logically questionable to assume a positive (or negative) deviation from the mean concentration at all small regions in the entire solution because that breaks the mass conservation rule. Therefore a positive deviation from the mean concentration must be compensated for by a negative deviation in another region to balance the numbers of each component. In other words, the random mixing model gives quite a reasonable statistical average over the entire solution although a deviation of concentration from the random mixing or fluctuation of concentration is an essential feature in the microscopic range.

In this work an equation is derived to determine the local concentration in solution from the maximum condition of the number of configurations in solution where the solution is separated into two hypothetical regions, a small region and the rest. The physical meaning of deviation of local concentration from the random mixing model and of the random mixing model itself is discussed based on results obtained from the calculations.

## BASIC EQUATION FOR LOCAL CONCENTRATION IN BINARY SOLUTION

It is instructive to derive an equation to determine a local concentration in a simple liquid solution consisting of  $N_1$  molecules of component 1 and  $N_2$  molecules of component 2 where both molar volumes are equal, i.e.

$V_1^0 = V_2^0$ . The solution is separated hypothetically into two regions, one is a small region with volume  $v$  containing  $n_1$  molecules of 1 and  $n_2$  of 2 and the other is the rest containing  $(N_1 - n_1)$  of 1 and  $(N_2 - n_2)$  of 2. The number of configurations for the separated solution  $w(n_1, n_2)$  is given by:

$$w(n_1, n_2) = [\{N_1!/(N_1 - n_1)!n_1!\} \{N_2!/(N_2 - n_2)!n_2!\}] \times [(n_1 + n_2)!/n_1!n_2!] \times [(N_1 + N_2 - n_1 - n_2)!/(N_1 - n_1)!(N_2 - n_2)!] \quad (1)$$

where the first square brackets indicate the number of ways to pick up or separate  $n_1$  molecules of 1 from  $N_1$  and  $n_2$  molecules of 2 from  $N_2$ , the second square brackets give the number of configurations in the small region consisting of  $n_1$  of 1 and  $n_2$  of 2, the last show the number of configurations in the rest of the solution containing  $(N_1 - n_1)$  of 1 and  $(N_2 - n_2)$  of 2. The total number of configurations  $w_{total}$  in the solution with no condition is

$$w_{total} = \{(N_1 + N_2)!/N_1!N_2!\} \quad (2)$$

The probability  $P(n_1, n_2)$  that the solution has a small region containing  $n_1$  molecules of 1 and  $n_2$  of 2 is

$$P(n_1, n_2) = w(n_1, n_2)/w_{total} \quad (3)$$

The maximum condition for  $P(n_1, n_2)$  with respect to  $n_1$  under a condition that  $n_2$  depends on  $n_1$  in the small region with a constant volume  $v$  is

$$\{\partial \ln P(n_1, n_2)/\partial n_1\}_{N_1, N_2, v} = \{\partial \ln w(n_1, n_2)/\partial n_1\}_{N_1, N_2, v} = 0 \quad (4)$$

It can be shown from equations (1) and (4) and the approximations  $N_1 \gg n_1$  and  $N_2 \gg n_2$  that

$$\ln(\psi_1^2 x_2^2/x_1^2 \psi_2^2) + 2k \ln(\psi_2/x_2) + k \ln(N_i/n_i) = 0 \quad (5)$$

where  $\psi_i = N_i/(N_1 + N_2)$ ,  $x_i = n_i/(n_1 + n_2)$ ,  $N_i = N_1 + N_2$ ,  $n_i = n_1 + n_2$  and  $k$  is defined by

$$k = \pm \{1 + (V_2^0/V_1^0)(\partial n_2/\partial n_1)_v\} \quad (6)$$

and in the case of  $V_1^0 = V_2^0$ ,  $k = \pm \{1 + (\partial n_2/\partial n_1)_v\}$ . Equation (5) with  $k=0$  is given by

$$\ln(\psi_1^2 x_2^2/x_1^2 \psi_2^2) = 0 \quad (7)$$

and therefore

$$x_1 = \psi_1$$

which is identical to that in the random mixing model. Although equation (1) is based on ideal mixing, it is still useful for mixtures showing a cluster formation or a non-random mixing, which will be discussed later.

### DERIVATION OF THE EQUATION FOR LOCAL CONCENTRATION IN POLYMER SOLUTION

The local concentration for a solution of polymer in solvent has been determined by a similar procedure to that in the simple liquid solution. The number of configurations,  $w_p$ , for a polymer solution separated hypothetically into two regions, one a small region containing  $n_2$  polymer molecules with  $r$  segments per molecule and  $n_1$  solvent molecules and the other a large region containing  $N_2 - n_2$  polymer molecules and  $N_1 - n_1$  solvent molecules, where  $N_2 \gg n_2$  and  $N_1 \gg n_1$ , is expressed

by:

$$w_p = [\{(N_2 r)!/(n_2 r)!(N_2 r - n_2 r)!\} \{N_1! / n_1! (N_1 - n_1)!\}] \times [\{(n_2 r + n_1)! / (n_2 r)! n_1!\} \{n_2 r / (n_2 r + n_1)\}^{n_2(r-1)-x}] \times \{(n_2 + x)!(n_1 + n_2)! / n_2!(n_1 + n_2 + x)!\} \times [\{(N_1^* - n_1 - n_2 r) / (N_1 - n_1)!(rN_2 - n_2 r)!\}] \times \{(N_2 - n_2)r / (N_1 - n_1 + (N_2 - n_2)r)\}^{(N_2 - n_2)(r-1)-y} \times \{(N_2 - n_2 + y)!(N_1 - n_1 + N_2 - n_2)! / (N_2 - n_2)!(N_1 - n_1 + N_2 - n_2 + y)!\} \quad (8)$$

where  $N_1^* = N_1 + N_2 r$  and  $x$  and  $y$  are parameters characterizing the flexibility of polymers in the small and large regions in solution, respectively, and are introduced in a previous work<sup>11</sup>. The first square brackets in equation (8) indicate the number of ways to separate  $n_2 r$  segments from  $N_2 r$  total segments for polymers of  $N_2$  and  $n_1$  solvents from  $N_1$  total solvents, the second square brackets show the number of configurations of  $n_2$  polymers with the flexibility parameter  $x$  and  $n_1$  solvents in the small region, and the third give the number of configurations of  $N_2 - n_2$  polymers with the flexibility parameter  $y$  and  $N_1 - n_1$  solvents. The maximum condition of equation (8) is given by

$$(\partial \ln w_p / \partial n_1)_{N_1, N_2, v} = \ln[\{\phi_1^2 X_2 (X_1 + X_2/r)(\phi_1 + \phi_2/r + \alpha \phi_1 \phi_2) / \{X_1^2 \phi_2 (\phi_1 + \phi_2/r) \times (X_1 + X_2/r + \alpha X_1 X_2)\} - \{(1-k)/r\} \times \ln[\{\phi_2 (\phi_1 + \phi_2/r + \alpha \phi_1 \phi_2)(r^{-1} + \alpha X_1)(X_1 + X_2/r) / \{X_2 (X_1 + X_2/r + \alpha X_1 X_2)(r^{-1} + \alpha \phi_1)(\phi_1 + \phi_2/r)\} \} + \alpha(1 - 2X_1 + kX_1^2) \ln\{(r^{-1} + \alpha X_1) / (X_1 + X_2/r + \alpha X_1 X_2)\} + \alpha(1 - 2\phi_2 - k\phi_1^2) \ln\{(r^{-1} + \alpha \phi_1) / (\phi_1 + \phi_2/r + \alpha \phi_1 \phi_2)\} + \alpha(1-k)(X_1 - \phi_1) + k\{(1-r^{-1})(\phi_2 - X_2) + \alpha X_1 X_2 - \alpha \phi_1 \phi_2\} + k \ln(\phi_2/X_2) + k \ln(N_1^*/n_1^*) = 0 \quad (9)$$

where  $n_1^* = n_1 + rn_2$ . The parameters  $x$  and  $y$  are defined using a constant  $\alpha$  by

$$x = \alpha rn_2 X_1 \quad (10)$$

and

$$y = \alpha r(N_2 - n_2)(N_1 - n_1) / \{(N_2 - n_2)r + (N_1 - n_1)\} \quad (11)$$

The parameters  $x$  and  $y$  are zero for flexible polymers and the values increase with an increasing rod-like character in polymer chains and are mentioned in more detail in the previous work<sup>11</sup>. The local volume fraction  $X_2$  for the polymer is defined by:

$$X_2 = rn_2 / (n_1 + rn_2) \quad (12)$$

where  $X_1 = 1 - X_2$ . The mean volume fraction  $\phi_2$  for the polymer is defined by:

$$\phi_2 = rN_2 / (N_1 + rN_2) \quad (13)$$

where  $\phi_1 = 1 - \phi_2$  and  $r$  is defined by  $r = V_2^0/V_1^0$ .

It is very interesting to derive an equation in the special case of equation (9). In the case of the solution of a flexible polymer,  $\alpha = 0$ , equation (9) reduces to

$$(\partial \ln w_p / \partial n_1)_{N_1, N_2, v, \alpha=0} = \ln(\phi_1^2 X_2 / X_1^2 \phi_2) + \{k - (1-k)/r\} \times \ln(\phi_2/X_2) + k(1 - r^{-1})(\phi_2 - X_2) + k \ln(N_1^*/n_1^*) = 0 \quad (14)$$

and in the special case of a solution of a flexible polymer  $\alpha = 0$  and  $k = 0$ , equation (9) reduces to a simpler equation:

$$(\partial \ln w_p / \partial n_1)_{N_1, N_2, v, \alpha = 0, k = 0} = \ln(\phi_1^2 X_2 / X_1^2 \phi_2) - r^{-1} \ln(\phi_2 / X_2) = 0 \quad (15)$$

It is obtained from equation (15) that

$$X_1 = \phi_1 \quad (16)$$

which is equal to that in the random mixing model. It is noteworthy that the random mixing model or  $X_1 = \phi_1$  is held in equation (9) if  $k \ln(N_i^*/n_i^*) = 0$  or if either  $k = 0$  or  $N_i^*/n_i^* = 1$  is satisfied. It is also pointed out that equation (9) with  $\alpha = 0$  and  $r = 1$  is equal to equation (5) for the simple liquid solution.

It is important to evaluate the value of  $k$  experimentally. It can be obtained from the thermodynamic equation that:

$$(dV_M)_{P,T} = (\partial V_M / \partial n_1)_{n_2} dn_1 + (\partial V_M / \partial n_2)_{n_1} dn_2 \quad (17)$$

and equation (17) under constant volume of solution  $dV_M = 0$  is expressed by:

$$(\partial n_2 / \partial n_1)_{V_M} = -(\partial V_M / \partial n_1)_{n_2} / (\partial V_M / \partial n_2)_{n_1} \quad (18)$$

In the case of an ideal solution where the excess volume of mixing  $\Delta V^E = 0$ , equation (18) is reduced to:

$$(\partial n_2 / \partial n_1)_{V_M} = -V_1^0 / V_2^0 \quad (19)$$

Then  $k$  in equation (6) in the small region is obtained by replacing  $V_M$  by  $v$  in equation (19) by

$$k = \pm \{ (V_2^0 / V_1^0) (\partial n_2 / \partial n_1)_v + 1 \} = 0 \quad (20)$$

It is found from equation (20) that the random mixing model holds in the polymer and simple liquid solutions when  $\Delta V^E = 0$ . Determination of  $k$  has been carried out using data of specific volume of solution. The partial molar volume of solvent 1 is obtained by

$$(\partial V_M / \partial n_1)_{n_2} = M_1 \{ v_m - w_2 (\partial v_m / \partial w_2) \} \quad (21)$$

and that for solute 2 is

$$(\partial V_M / \partial n_2)_{n_1} = M_2 \{ v_m + w_1 (\partial v_m / \partial w_2) \} \quad (22)$$

where  $v_m = V_M / (m_1 + m_2)$  and  $m_i$  is the mass of component  $i$ ,  $w_i$  is the weight fraction of  $i$ . The value of  $k$  is given by

$$k = \pm [1 - (v_2^0 / v_1^0) \{ v_m - w_2 (\partial v_m / \partial w_2) \} / \{ v_m + w_1 (\partial v_m / \partial w_2) \}] \quad (23)$$

It is useful to rewrite equation (23) using mole fraction  $x_i$  for simple liquid mixtures and volume fraction in polymer solution, which are given by:

$$k = \pm \{ 1 - (v_2^0 / v_1^0) + (v_2^0 / v_1^0) [x_1 M_1 / (x_1 M_1 + x_2 M_2) + \{ (\partial \ln v_m / \partial x_2) (x_1 M_1 + x_2 M_2)^2 / M_1 M_2 \}^{-1}]^{-1} \} \quad (24)$$

and

$$k = \pm \{ 1 - (v_2^0 / v_1^0) + (v_2^0 / v_1^0) [(\phi_1 / v_1^0) / (\phi_1 / v_1^0 + \phi_2 / v_2^0) + \{ (\partial \ln v_m / \partial \phi_2) \times v_1^0 v_2^0 (\phi_1 / v_1^0 + \phi_2 / v_2^0)^2 \}^{-1}]^{-1} \} \quad (25)$$

where  $v_i^0$  is the specific volume of  $i$  and  $v_i^0 = V_i^0 / M_i$ .

In a previous work we obtained a semi-empirical equation for the specific volumes and excess volume in simple liquid mixtures and polymer solutions, which is

given by<sup>12</sup>

$$v_m = v_1^0 (v_2^0 / v_1^0)^{Y(x_2)} \quad (26)$$

where

$$Y(x_2) = 2^n / (2^n - 1) - (2 - x_2)^n (2^n - 1)^{-1} \quad (27)$$

In the case of polymer solution the mole fraction is converted into the volume fraction  $\phi_i$  in equation (26). It is interesting to derive the equation for  $k$  at a concentration  $x_1 = 0.5$  or  $\phi_1 = 0.5$  using equations (24), (25) and (26), that is:

$$k(x_1 = 0.5) = \pm [1 - (v_2^0 / v_1^0) + (v_2^0 / v_1^0) \{ M_1 / (M_1 + M_2) \} / 2 + \{ n(1.5)^{n-1} / (2^n - 1) \} \{ \ln(v_2^0 / v_1^0) \} \times 0.25 (M_1 + M_2)^2 / M_1 M_2 ]^{-1} \quad (28)$$

where it is convenient to use  $k_+$  for the positive part of  $k$  in equation (28) (see *Figure 1*) and

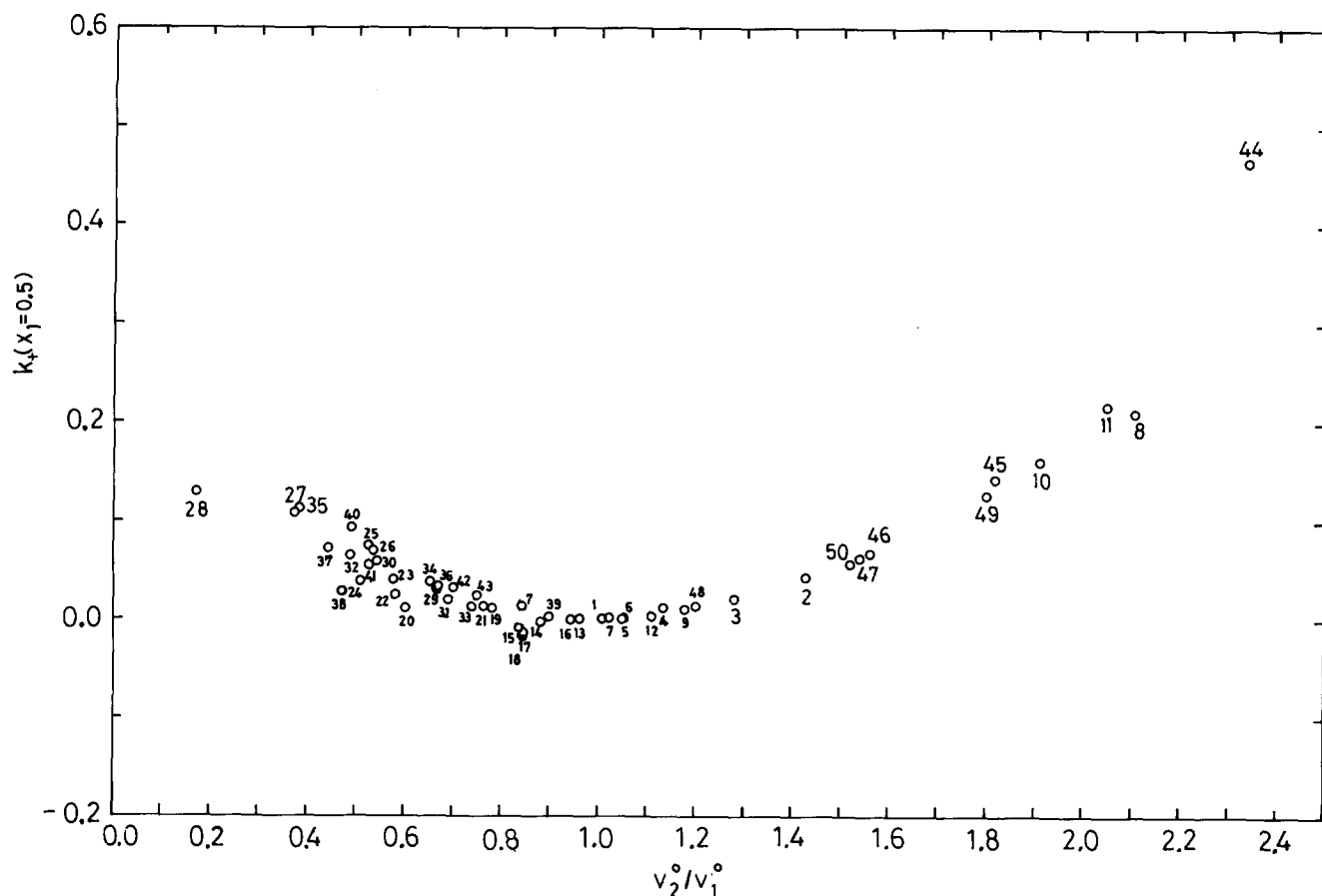
$$k(\phi_1 = 0.5) = \pm [1 - (v_2^0 / v_1^0) + (v_2^0 / v_1^0) \{ 1 + (v_1^0 / v_2^0) \}^{-1} + \{ (1.5)^{n-1} n / (2^n - 1) \} \{ \ln(v_2^0 / v_1^0) \} \times 0.25 (v_1^0 + v_2^0)^2 / v_1^0 v_2^0 ]^{-1} \quad (29)$$

## RESULTS

Values of  $k_+$  calculated using equations (28) and (29) based on the experimental data are listed in *Table 1* and are plotted against  $v_2^0 / v_1^0$  in *Figure 1* where values of  $k_+$  are nearly equal to zero around  $v_2^0 / v_1^0 = 1.0$  and increase with increase or decrease of  $v_2^0 / v_1^0$  and values of  $k$  in polymer solutions are around  $\pm 0.0018$ . Values of local concentrations calculated by equation (5) for various values of  $k$  are shown for simple liquid solutions in *Figure 2*. At each concentration  $k$  has two values, one positive and the other negative, and  $k > 0$  corresponds to positive fluctuation around the mean or macroscopic concentration expressed by  $x_1 - \psi_1 > 0$  and  $k < 0$  to negative fluctuation. Therefore the absolute value of  $k$  gives a measure of maximum fluctuation around the mean concentration. The local volume fraction  $X_1$  for solvent in the flexible polymer solution is calculated by equation (14) and is shown in *Figure 3*. The molecular weight or  $r$  dependence and  $k$  and  $N_i^*/n_i^*$  dependence of the local concentration are shown in *Figures 4, 5* and *6*, where values of  $X_1$  increase with increase of  $|k|$  and  $\ln(N_i^*/n_i^*)$  linearly, while  $X_1$  approaches a constant value with increase of  $\ln r$ .

## DISCUSSION

It is found in this work that a deviation of local concentration from the mean or macroscopic concentration is attributed to a term  $k \ln(N_i/n_i)$  in equations (5) and (9) where values of  $k$  can be determined from the partial volumes of solute and solvent, while  $N_i/n_i$  corresponds to the magnification of the microscope, which can be set arbitrarily. If we observe the solution by increasing the magnification of the microscope, the molecules in the field of vision of the microscope will move dynamically and continually. For example, some molecules will move into the field and others out, some molecules collide with others and some vibrate around their positions. On the other hand, if we observe various regions in solution by keeping the magnification constant, it will be found that



**Figure 1** Plot of  $k_+$  versus  $v_2^0/v_1^0$  in the simple liquid solutions calculated using equations (28) and (29). Data are given in Table 1 and are taken from ref. 12

the concentrations in the regions differ slightly from the mean concentration and some concentrations are higher than the mean one and others are lower. It is very important to discuss these behaviours based on the present work. Equation (6) can be rewritten using  $r = V_2^0/V_1^0$  as

$$k = \pm \{ \partial(n_2 r + n_1) / \partial n_1 \}_v \quad (30)$$

where  $(n_2 r + n_1) = n_t^*$  is the total number of molecules and segments in the small region of volume  $v$ . If there is no excess volume of mixing, i.e.  $\Delta V^E = 0$ , then  $k$  is equal to zero as shown in equation (20) and because  $n_t = v/\bar{v}$  is constant where  $\bar{v}$  is the molecular volume. In a solution where  $\Delta V^E \neq 0$ ,  $n_t$  in  $v$  is not constant as is discussed below. An essential difference between the solutions with  $\Delta V^E = 0$  and  $\Delta V^E \neq 0$  is the rigidity or compressibility of molecules and segments in solution. In the ideal solution with  $\Delta V^E = 0$ , the molecules are assumed to be perfectly rigid balls with zero compressibility and therefore the number of molecules in  $v$  does not change by the introduction of molecules into  $v$ , while in the solution where  $\Delta V^E \neq 0$ , the molecules are compressible and therefore the molecules moving, vibrating and colliding in solution with thermal energy can produce free spaces through their dynamic motions and consequently number fluctuation and concentration fluctuation occur in solution where the mean number of molecules in  $v$  is given by

$$n_{\text{mean}} = (N_1/V_1)v \quad (31)$$

where  $V_1$  is the total volume of solution.

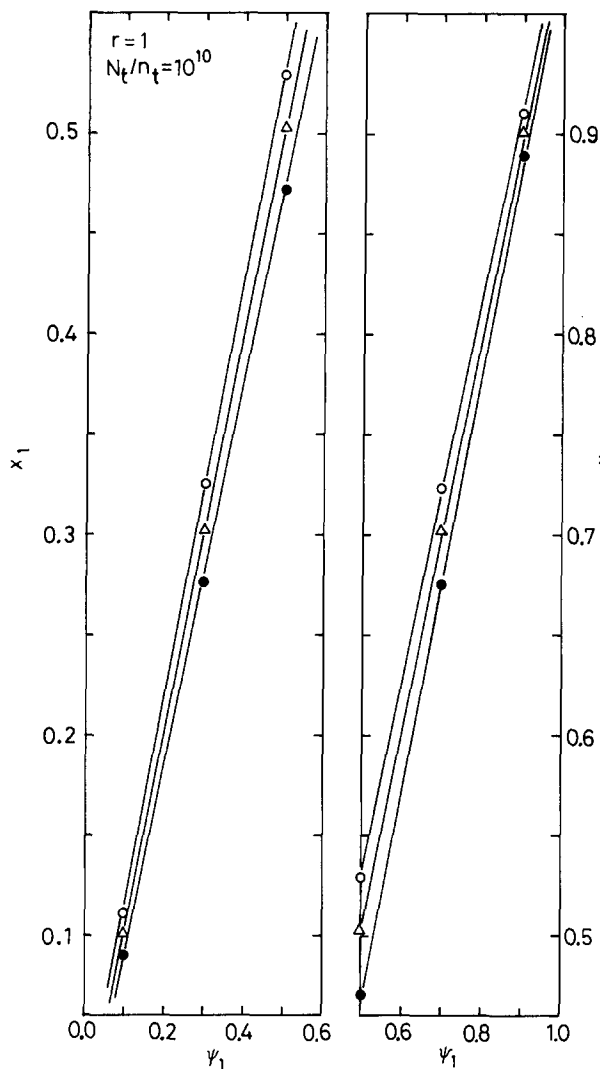
It is interesting to discuss the physical meaning of positive and negative values of  $k$  in equation (30). The positive value of  $(\partial n_t / \partial n_1)_v > 0$  in equation (30) indicates two cases where  $(\partial n_1 > 0, \partial n_t > 0)$  and  $(\partial n_1 < 0, \partial n_t < 0)$  and  $k$  has two values and four cases. Among these cases positive  $k = +(\partial n_t / \partial n_1)_v > 0$  for  $(\partial n_1 > 0, \partial n_t > 0)$  and negative  $k = -(\partial n_t / \partial n_1)_v < 0$  for  $(\partial n_1 < 0, \partial n_t < 0)$  are interesting physically. It is found in these calculations that the positive  $k$  corresponds to positive fluctuation or  $X_1 > \phi_1$  in Figure 3 and negative  $k$  to negative fluctuation. In the case of  $k > 0$  and  $(\partial n_1 > 0, \partial n_t > 0)$ , the number of molecules of 1,  $n_1$ , in the small region tends to increase and the concentration of 1,  $X_1$ , becomes higher than the mean value  $\phi_1$  (positive fluctuation). If the process of  $k > 0$  occurs in the region continuously, then both the total number of molecules  $n_t$  and  $n_1$  are greater than the mean  $n_{\text{mean}}$  and  $n_{\text{mean}}\phi_1$ , respectively. Further introduction of molecules of 1 into the region follows a decrease of  $n_t$  and  $n_1$  because the region is unstable thermodynamically. This process corresponds to  $k = -(\partial n_t / \partial n_1)_v < 0$  and  $(\partial n_1 < 0, \partial n_t < 0)$  and leads to a negative concentration fluctuation. It is true that the positive and negative concentration fluctuations in various regions in solution occur under a condition where the mass conservation rule is held. In other words, an occurrence of positive fluctuation in some region is responsible for negative fluctuation at another near region and the average of fluctuation around the mean concentration over the entire solution must be zero. In this work the values of  $k$  are distributed over the solution in the range of negative  $k$  to positive  $k$  and the value of  $k$  averaged over

**Table 1** Values of  $k$  in simple liquid and polymer solutions calculated using equations (24) and (25) based on the experimental data list in ref. 12

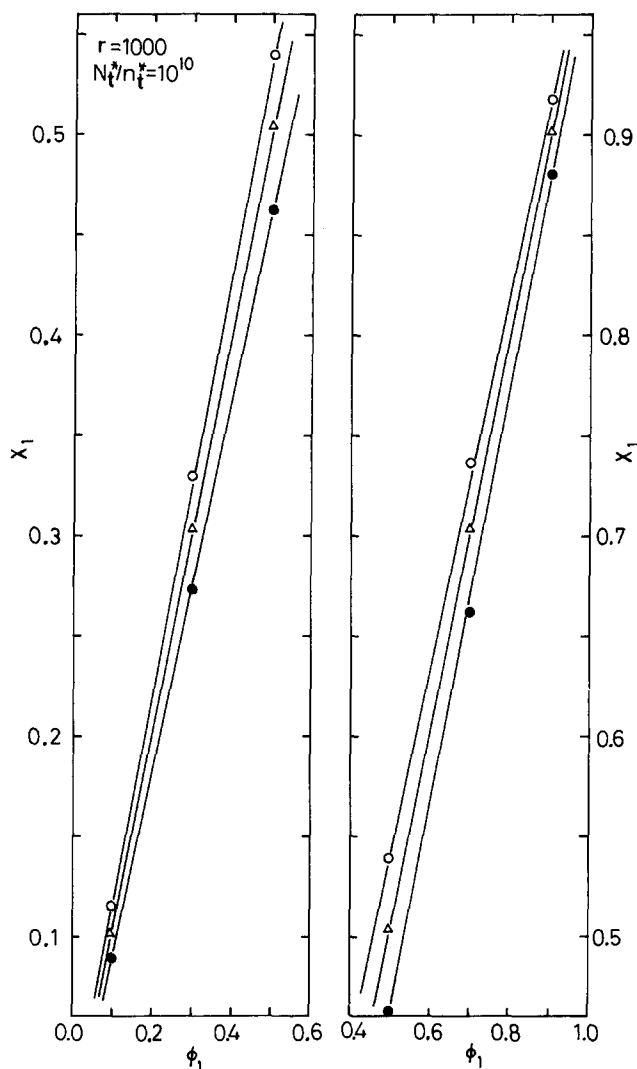
Solute (2)	$M_2$ (g mol <sup>-1</sup> )	Solvent (1)	$M_1$ (g mol <sup>-1</sup> )	$v_1^0$ (cm <sup>3</sup> g <sup>-1</sup> )	$v_2^0/v_1^0$	$n$	$k_+$ <sup>a</sup> ( $x_1=0.5$ )	No. (point on Figure 1)
C <sub>2</sub> H <sub>6</sub>	30.07	C <sub>2</sub> H <sub>4</sub>	28.054	1.7279	1.0113	4.91	-0.0019	1
C <sub>6</sub> H <sub>6</sub>	78.114	CS <sub>2</sub>	76.131	0.7962	1.438	1.84	0.0426	2
n-C <sub>7</sub> H <sub>16</sub>	100.205	C <sub>6</sub> H <sub>6</sub>	78.114	1.1445	1.2862	2.38	0.0229	3
n-C <sub>16</sub> H <sub>34</sub>	226.448	C <sub>6</sub> H <sub>6</sub>	78.114	1.1445	1.1351	5.31	0.0111	4
Cyclo-C <sub>8</sub> H <sub>16</sub>	112.216	C <sub>6</sub> H <sub>6</sub>	78.114	1.1445	1.0515	3.59	-0.0013	6
<i>p</i> -xylene	106.168	C <sub>6</sub> H <sub>6</sub>	78.114	1.1445	1.020	3.22	-0.0004	7
n-C <sub>14</sub> H <sub>30</sub>	198.394	C <sub>6</sub> F <sub>6</sub>	186.056	0.6228	2.1043	2.48	0.2089	8
<i>m</i> -xylene	106.168	Aniline	93.129	0.9783	1.1829	1.67	0.0098	9
n-C <sub>6</sub> H <sub>14</sub>	86.178	CS <sub>2</sub>	76.131	0.7962	1.917	2.38	0.1598	10
n-C <sub>16</sub> H <sub>34</sub>	226.448	CCl <sub>4</sub>	153.823	0.6312	2.049	3.29	0.2167	11
Cyclo-C <sub>8</sub> H <sub>16</sub>	112.216	ClC <sub>6</sub> H <sub>5</sub>	112.559	0.9083	1.1104	1.55	0.0034	12
n-C <sub>7</sub> H <sub>16</sub>	100.205	n-C <sub>6</sub> H <sub>14</sub>	86.178	1.5267	0.96423	1.45	-0.00002	13
n-C <sub>11</sub> H <sub>24</sub>	156.313	n-C <sub>6</sub> H <sub>14</sub>	86.178	1.5267	0.8852	2.73	-0.0030	14
n-C <sub>16</sub> H <sub>34</sub>	226.448	n-C <sub>6</sub> H <sub>14</sub>	86.178	1.6074	0.8341	4.01	-0.0094	15
n-C <sub>9</sub> H <sub>20</sub>	128.259	n-C <sub>7</sub> H <sub>16</sub>	100.205	1.4721	0.9461	1.71	-0.0002	16
n-C <sub>20</sub> H <sub>42</sub>	282.556	n-C <sub>7</sub> H <sub>16</sub>	100.205	1.5619	0.8475	4.20	-0.0120	17
n-C <sub>36</sub> H <sub>74</sub>	506.99	n-C <sub>9</sub> H <sub>20</sub>	128.259	1.5851	0.8395	5.41	-0.0209	18
C <sub>2</sub> H <sub>4</sub>	28.054	CH <sub>4</sub>	16.043	2.3053	0.6623	2.23	0.0188	19
C <sub>3</sub> H <sub>8</sub>	44.097	CH <sub>4</sub>	16.043	2.3389	0.6024	3.81	0.0104	20
Cyclo-C <sub>6</sub> H <sub>12</sub>	84.162	C(CH <sub>3</sub> ) <sub>4</sub>	72.151	1.6358	0.7669	1.47	0.0138	21
BrC <sub>6</sub> H <sub>5</sub>	157.010	C <sub>6</sub> H <sub>6</sub>	78.114	1.1578	0.5854	2.28	0.0249	22
BrC <sub>6</sub> H <sub>5</sub>	157.010	CH <sub>3</sub> C <sub>6</sub> H <sub>5</sub>	92.141	1.1726	0.5780	1.79	0.0393	23
HBr	80.912	HCl	36.461	0.8563	0.5095	2.38	0.03855	24
1,2-Cl <sub>2</sub> C <sub>6</sub> H <sub>4</sub>	147.004	2,2,4TMP	114.232	1.4539	0.5289	0.906	0.0733	25
1,3-Cl <sub>2</sub> C <sub>6</sub> H <sub>4</sub>	147.004	2,2,4TMP	114.232	1.4539	0.5362	0.83	0.0715	26
CCl <sub>4</sub>	153.823	C(CH <sub>3</sub> ) <sub>4</sub>	72.151	1.6358	0.3744	1.83	0.1077	27
Kr	83.800	CH <sub>4</sub>	16.043	2.4085	0.1700	3.37	0.1286	28
O <sub>2</sub>	31.999	N <sub>2</sub>	28.013	1.2359	0.6700	1.0	0.0325	29
Ar	39.948	N <sub>2</sub>	28.013	1.2887	0.5477	1.27	0.0604	30
Xe	131.300	Kr	83.800	0.4862	0.6983	2.34	0.0206	31
CCl <sub>4</sub>	153.823	CycloC <sub>6</sub> H <sub>12</sub>	84.162	1.292	0.4885	1.69	0.06509	32
BrC <sub>6</sub> H <sub>5</sub>	157.01	ClC <sub>6</sub> H <sub>5</sub>	112.559	0.9155	0.7403	1.54	0.0138	33
CH <sub>3</sub> I	141.939	CHCl <sub>3</sub>	119.373	0.6759	0.6532	0.874	0.0370	34
CH <sub>3</sub> I	141.939	C <sub>6</sub> H <sub>6</sub>	78.114	1.1446	0.3857	1.286	0.1199	35
C <sub>6</sub> H <sub>6</sub>	78.114	C(CH <sub>3</sub> ) <sub>4</sub>	72.151	1.6359	0.6788	0.81	0.0321	36
CCl <sub>4</sub>	153.823	Diethyl ether	74.123	1.4124	0.4469	2.07	0.0719	37
CHCl <sub>3</sub>	119.378	Diethyl ether	74.123	1.4124	0.4786	1.45	0.0272	38
C <sub>5</sub> H <sub>5</sub> N	79.102	C <sub>6</sub> H <sub>6</sub>	78.114	1.1445	0.8982	1.14	0.00248	39
CHCl <sub>3</sub>	119.378	(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N	101.193	1.3545	0.4891	0.74	0.0922	40
1,2Cl <sub>2</sub> C <sub>6</sub> H <sub>4</sub>	147.004	n-C <sub>8</sub> H <sub>18</sub>	163.541	1.4317	0.6345	-0.20	0.05517	41
CH <sub>3</sub> I	141.939	CCl <sub>4</sub>	153.823	0.6312	0.6995	0.20	0.03278	42
C <sub>6</sub> H <sub>6</sub>	78.114	n-C <sub>6</sub> H <sub>14</sub>	86.178	1.5267	0.7497	0.12	0.0241	43
HCl	36.461	Xe	131.300	0.3669	2.343	-1.06	0.4652	44
C <sub>6</sub> H <sub>6</sub>	78.114	CCl <sub>4</sub>	153.823	0.6311	1.814	-0.10	0.1403	45
CycloC <sub>8</sub> H <sub>16</sub>	112.216	1,2Cl <sub>2</sub> C <sub>6</sub> H <sub>4</sub>	147.004	0.7690	1.5628	0.964	0.0662	46
CycloC <sub>8</sub> H <sub>16</sub>	112.216	1,3Cl <sub>2</sub> C <sub>6</sub> H <sub>4</sub>	147.004	0.7795	1.5417	0.966	0.0621	47
CH <sub>2</sub> Cl <sub>2</sub>	84.933	CCl <sub>4</sub>	153.823	0.6312	1.2036	-0.196	0.0141	48
<i>o</i> -xylene	106.168	CCl <sub>4</sub>	153.823	0.6312	1.8085	0.78	0.1260	49
C <sub>5</sub> H <sub>5</sub> N	79.102	CHCl <sub>3</sub>	119.378	0.6864	1.5201	0.37	0.0565	50
PIB <sup>b</sup>	4.0 × 10 <sup>4</sup>	CycloC <sub>6</sub> H <sub>12</sub>	84.162	1.2921	0.8441	1.35	-0.0011	
PIB <sup>b</sup>	4.0 × 10 <sup>4</sup>	n-C <sub>6</sub> H <sub>14</sub>	86.178	1.5267	0.7143	1.80	-0.0042	
PS <sup>b</sup>	5.1 × 10 <sup>4</sup>	MEK	72.107	1.2502	0.7468	1.76	-0.0031	
PS <sup>b</sup>	5.1 × 10 <sup>4</sup>	C <sub>2</sub> H <sub>5</sub> C <sub>6</sub> H <sub>5</sub>	106.168	1.1592	0.8054	1.49	-0.0019	
PDMS <sup>b</sup>	10 <sup>5</sup>	C <sub>6</sub> H <sub>6</sub>	78.114	1.1445	0.9011	1.25	-0.0005	
PIB <sup>b</sup>	4.0 × 10 <sup>4</sup>	C <sub>6</sub> H <sub>6</sub>	78.114	1.1445	0.9529	0.25	0.0012	
NR <sup>b</sup>	4.0 × 10 <sup>4</sup>	C <sub>6</sub> H <sub>6</sub>	78.114	1.1445	0.9569	0.83	0.0002	
PDMS <sup>b</sup>	10 <sup>5</sup>	ClC <sub>6</sub> H <sub>5</sub>	112.559	0.9415	1.0952	0.20	-0.0024	

<sup>a</sup>  $k_+ = +\{1 + (V_2^0/V_1^0)(\partial n_2/\partial n_1)_v\}$ 
<sup>b</sup> In the case of polymer solutions  $k(\phi_1=0.5)$ . The data are not plotted in Figure 1 to avoid confusion

2,2,4TMP, 2,2,4-trimethylpentane; PIB, polyisobutylene; PS, polystyrene; PDMS, poly(dimethylsiloxane); NR, natural rubber; MEK, methyl ethyl ketone



**Figure 2** Local mole fraction of component 1,  $x_1$ , versus mean mole fraction of 1,  $\psi_1$ , in the simple liquid solution calculated using equation (5) with  $N_1/n_1 = 10^{10}$  and various values of  $k$ : (○)  $k=0.01$ ; (△)  $k=0.001$ ; (●)  $k=-0.01$



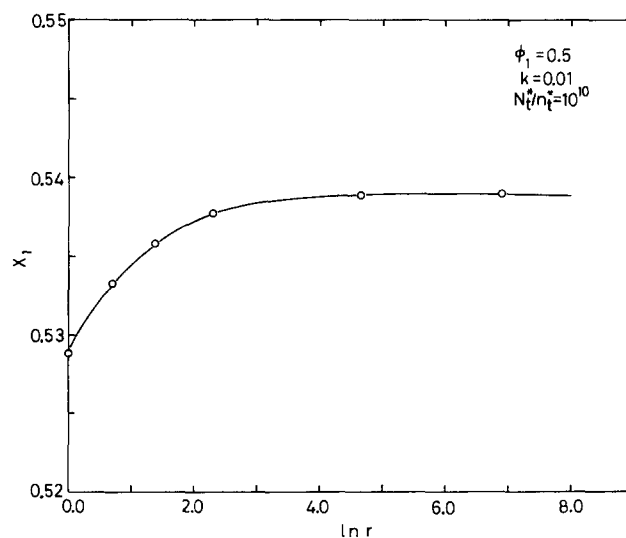
**Figure 3** Local volume fraction of solvent 1,  $X_1$  versus mean volume fraction of 1,  $\phi_1$ , in polymer solutions calculated using equation (14) with  $r=1000$  segments per polymer and  $N_1^*/n_1^* = 10^{10}$  and various values of  $k$ : (○)  $k=0.01$ ; (△)  $k=0.001$ ; (●)  $k=-0.01$

the solution must be zero from the condition that the mass conservation rule is held.

It is very important to examine whether equation (1) can be applied to any type of solution, such as a non-ideal mixture with non-zero enthalpy of mixing  $\Delta H_M \neq 0$ . Since the cluster formation in solution comes from an asymmetry of molecular interaction between solvent-solvent and solute-solute and is related to  $\Delta H_M$ , the number of configurations in a non-ideal mixture can be estimated by taking into account the effect of cluster formation. The number of configurations in the non-ideal mixture is expressed by the equation:

$$w_{ni}(n_1, n_2) = \{N_1! / (N_1 - n_1)! n_1!\} \{N_2! / (N_2 - n_2)! n_2!\} \\ \times \{(n_1 + n_2 - c_1 - c_2)! / (n_1 - c_1)! (n_2 - c_2)!\} \\ \times \{(N_1 + N_2 - n_1 - n_2 - d_1 - d_2)! / \\ (N_1 - n_1 - d_1)! (N_2 - n_2 - d_2)!\} \quad (32)$$

where  $c_1$  and  $c_2$  are the decrease in number due to the cluster formation of molecules 1 and 2, respectively, in the small region, while  $d_1$  and  $d_2$  are the decrease in number due to the clusters in the rest. It is important to



**Figure 4** Plot of  $X_1$  versus  $\ln r$  in a simple liquid and polymer solution calculated using equation (14) at  $\phi_1=0.5$ ,  $k=0.01$  and  $N_1^*/n_1^* = 10^{10}$

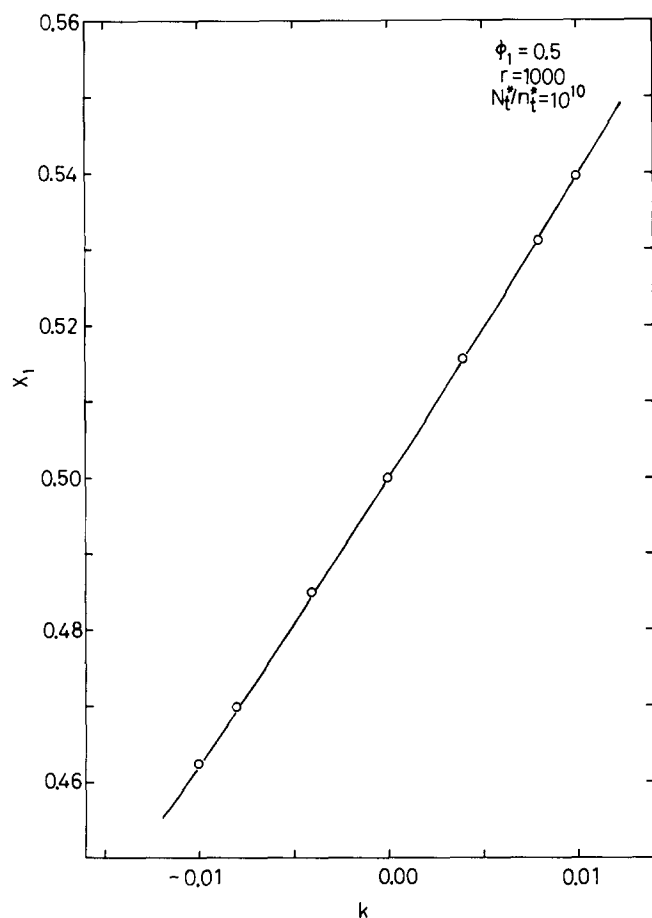


Figure 5 Plot of  $X_1$  versus  $k$  in polymer solution calculated using equation (14) at  $\phi_1=0.5$ ,  $r=1000$  and  $N_t^*/n_t^*=10^{10}$

point out that equation (32) is valid only while the clusters are stable. In general the clusters are not permanent, except for the products of a chemical reaction, and break up easily to their original molecules which can move as independently as in the ideal mixture. Therefore time-averaged values of  $c_i$  and  $d_i$  over times much longer than the stable or living times of cluster are approximately zero for each molecule. A main difference between the non-ideal mixture and the ideal mixture with respect to the behaviour of molecular motion is a difference of the time from a collision of molecules to separation to individual molecules. The time in the non-ideal mixture is longer than that in the ideal mixture. Equation (32) may be applicable to a micelle solution where the micelles are stable in solution over a long time. The present work was based on the assumption that there is no significant difference in the number of configurations between an ideal mixture and a non-ideal mixture with a weak clustering tendency.

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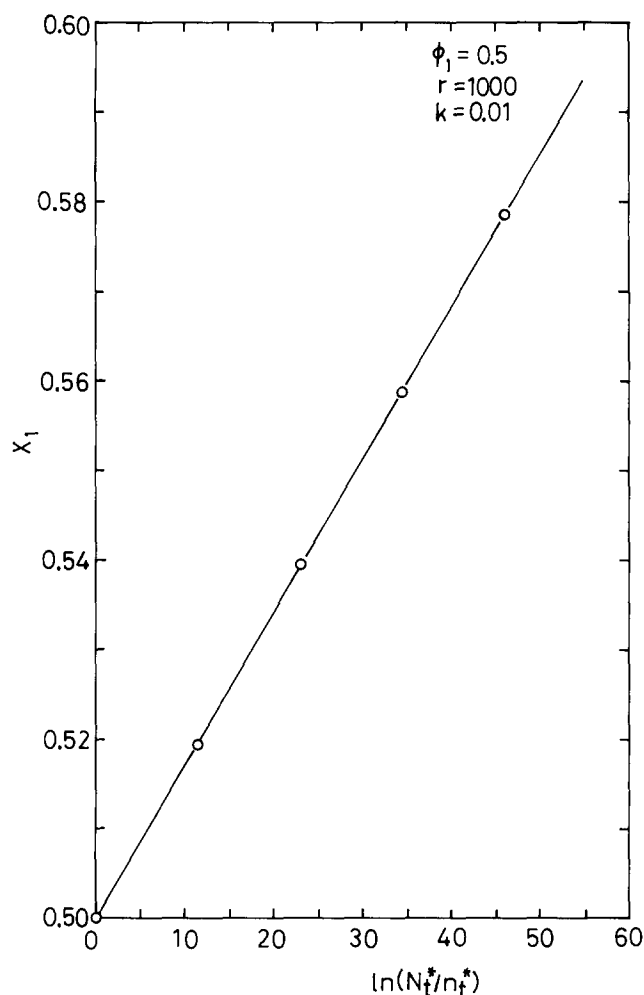


Figure 6 Plot of  $X_1$  versus  $\ln(N_t^*/n_t^*)$  in polymer solution calculated using equation (14) at  $\phi_1=0.5$ ,  $r=1000$  and  $k=0.01$

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#### REFERENCES

- 1 Wilson, G. M. *J. Am. Chem. Soc.* 1964, **86**, 127
- 2 Abrams, D. S. and Prausnitz, J. M. *Am. Inst. Chem. Eng.* 1975, **21**, 116
- 3 Renuncio, J. A. R. and Prausnitz, J. M. *Macromolecules* 1976, **9**, 898
- 4 Brandani, V. *Macromolecules* 1979, **12**, 883
- 5 Rubio, R. G. and Renuncio, J. A. R. *Macromolecules* 1980, **13**, 1508
- 6 Koningsveld, R. and Kleintjens, L. A. *Macromolecules* 1971, **4**, 637
- 7 Fixman, M. *J. Chem. Phys.* 1961, **35**, 889
- 8 Kirkwood, J. G. and Buff, F. P. *J. Chem. Phys.* 1951, **19**, 774
- 9 Saeki, S., Tsubokawa, M. and Yamaguchi, T. *Macromolecules* 1987, **20**, 2930
- 10 Saeki, S., Tsubokawa, M. and Yamaguchi, T. *Macromolecules* 1988, **21**, 2210
- 11 Saeki, S. *Polymer* 1993, **34**, 4118
- 12 Saeki, S., Tsubokawa, M., Yamanaka, J. and Yamaguchi, T. *Polymer* 1992, **33**, 2382