Isotonic mixing: a novel technique for observing polymer–polymer interaction

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(*Received 5 March 1990; revised 8 May 1990; accepted 4 June 1990*)

When two isotonic polymer solutions are mixed together, the osmotic pressure of the mixture may remain unchanged, in an ideal system, or may show a change, indicating non-ideality arising from polymer–polymer interaction. The excess osmotic pressure should be an excellent empirical measure of interaction between the two polymers, and may be a guide to phase separation in the ternary system.

(Keywords: isotonic solutions; isotonic mixing; excess osmotic pressure; isotonic excess; polymer–polymer interaction)

INTRODUCTION

The interaction between two polymers in a common solvent is of great interest. Such interactions can be repulsive or attractive and are considered to be responsible for phase separation[1–3] in ternary systems consisting of two polymers and a mutual solvent, resulting in incompatibility, coacervation, gelation, aggregation, etc. Considerable theoretical and experimental work has been done in this field. In this communication we propose a new osmometric technique, which should enable one almost to 'see' polymer–polymer interaction directly and should also provide a useful empirical measure of this interaction.

THE TECHNIQUE

The essential step in this method is to prepare two exactly isotonic solutions—one of polymer 2 and the other of polymer 3, to be designated as I_2 and I_3 respectively—in a mutual solvent (1). It should be possible to accomplish this by preparing, in the first instance, two solutions of nearly equal osmotic pressures by trial and error, and then dialysing one of the solutions against the other until equilibrium is attained, which should be monitored by osmotic pressure measurement. Let these exactly isotonic solutions be designated as I_2 and I_3 respectively. In the next step, a series of mixtures of I_2 and I_3, referred to hereafter as isotonic mixtures, are prepared, and the osmotic pressure of each mixture is determined. Any difference between the pressures Π of either I_2 or I_3 and Π_m of an isotonic mixture will directly show the presence of some kind of interaction between polymer 2 and polymer 3. Defining an excess osmotic pressure Π^E as:

$$\Pi^E = \Pi_m - \Pi \qquad (1)$$

we can see that Π^E will serve as a directly visible empirical parameter of polymer–polymer interaction, as shown schematically in *Figure 1*. A plot of Π^E against the weight fraction of either component in the isotonic mixture, as shown schematically in *Figure 2*, may exhibit one of the features of Raoult's vapour pressure plots. There may be no deviation, indicating absence of an overall interaction and no phase separation in the ternary system. A negative deviation, on the other hand, would indicate attraction, which may lead to coacervation or some other complex phase behaviour. Experimentally, accuracy could be ensured in a differential type of measurement in which one of the isotonic solutions, I_2 or I_3, is poised against an isotonic mixture, $I_2 + I_3$, as shown in *Figure 1*. Moreover, in differential osmometry one can deal with very high concentrations. Modern osmometers, using piezoelectric devices, afford quick measurement, but since each solution is measured against the solvent one must be very sure about the precision of two separate measurements, the difference of which is the desired quantity.

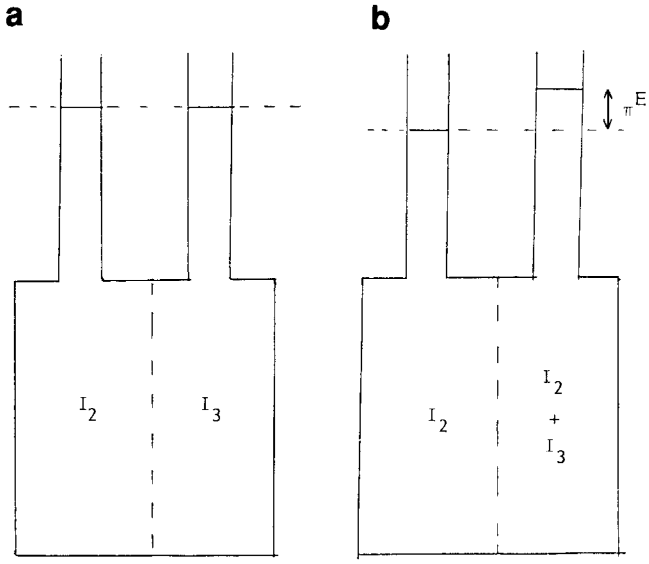

Figure 1 Schematic representation of excess osmotic pressure in a differential osmometry set-up. In (a) two isotonic solutions, I_2 and I_3, are shown evenly poised against each other across the membrane. In (b), a mixture of I_2 and I_3 is unevenly poised against either I_2 or I_3, showing a positive excess osmotic pressure Π^E

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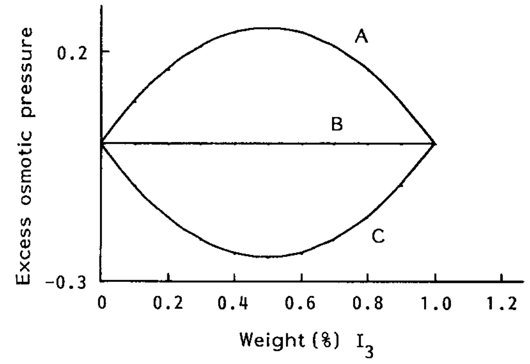

Figure 2 Schematic plots of excess osmotic pressure against the composition of the isotonic mixture, $I_2 + I_3$. Curves A and C represent positive and negative deviations, respectively, from ideal behaviour as represented by B

THERMODYNAMIC SIGNIFICANCE OF EXCESS OSMOTIC PRESSURE

Thermodynamics specifically for isotonic mixing does not seem to exist. Without making any attempt to fill that gap we intend to relate the purely empirical concept of excess osmotic pressure, as defined by equation (1), to some basic ideas of thermodynamics. It may be pointed out that the excess osmotic pressure Π^E as defined by equation (1) (which will henceforth be conveniently referred to as isotonic excess) is basically different from the commonly understood excess quantity, which is the difference between the experimentally observed osmotic pressure of a general ternary mixture and a somewhat dubiously calculated average of the osmotic pressures of two binary solutions. The isotonic excess, on the other hand, has an unambiguous basis, which is the common isotonic pressure of the component solutions. There may be a more fundamental feature to the isotonic excess. As Scott[2] pointed out, the binary solvent–polymer interaction parameters (1–2 and 1–3) are made up of both entropic and enthalpic contributions, whereas the polymer–polymer interaction (2–3) is entirely a heat contribution. It is quite possible that in isotonic mixing the entropic contributions largely cancel out and Π^E, the isotonic excess, results from the heat contribution. This suggestion is amenable to experimental verification. It should be emphasized that the empirical quantity Π^E is not the computed value of $\Pi_{\text{ternary}} - \sum \Pi_{\text{binary}}$.

Isotonic excess in terms of activity coefficients

Let the compositions of two isotonic solutions be:

$$I_2 = 1 \text{ ml solvent} + C'_2 \text{ g of polymer 2} \qquad (2)$$

$$I_3 = 1 \text{ ml solvent} + C'_3 \text{ g of polymer 3} \qquad (3)$$

Now the composition of the isotonic mixture can be expressed in the general form, $I_m = f_2 I_2 + f_3 I_3$, which may be expressed as:

$$I_m = 1 \text{ ml solvent} + f_2 C'_2 \text{ g of polymer 2} + f_3 C'_3 \text{ g of polymer 3} \qquad (4)$$

where f_2 and f_3 are positive fractions such that $f_2 + f_3 = 1$. It may be stated here that in this discussion C' will stand for concentration in isotonic solutions and their mixtures, while C will be used in general cases.

The chemical potentials of the solvent being equal in I_2 and I_3, we may write, using common symbols:

$$\mu_1(I_2) = \mu_1(I_3) = \mu_1 \qquad (5)$$

$$\mu_1 = \mu_1(I_2) = \mu_1^* + RT \ln x_1(I_2) + RT \ln y_1(I_2) \qquad (6)$$

$$\mu_1 = \mu_1(I_3) = \mu_1^* + RT \ln x_1(I_3) + RT \ln y_1(I_3) \qquad (7)$$

For the isotonic ternary mixture, I_m:

$$\mu_1 = \mu_1(I_m) = \mu_1^* + RT \ln x_1(I_m) + RT \ln y_1(I_m) \qquad (8)$$

The solvent mole fractions in the various solutions are given by:

$$x_1(I_2) = \frac{d_1/M_1}{d_1/M_1 + C'_2/M_2} \qquad (9)$$

$$x_1(I_3) = \frac{d_1/M_1}{d_1/M_1 + C'_3/M_3} \qquad (10)$$

$$x_1(I_m) = \frac{d_1/M_1}{d_1/M_1 + f_2C'_2/M_2 + f_3C'_3/M_3} \qquad (11)$$

where d_1 is the density of the solvent and M_1, M_2 and M_3 are molecular weights of the solvent and solutes.

Now, defining an excess isotonic solvent chemical potential μ_1^E as:

$$\mu_1^E = \mu_1(I_m) - \mu_1$$

we have from (6):

$$\mu_1^E = \mu_1(I_m) - f_2\mu_1(I_2) - f_3\mu_1(I_3)$$

and from (7) to (11):

$$\mu_1^E = RT \ln\left(\frac{(d_1/M_1 + C'_2/M_2)^{f_2}(d_1/M_1 + C'_3/M_3)^{f_3}}{d_1/M_1 + f_2C'_2/M_2 + f_3C'_3/M_3}\right) + RT \ln\left(\frac{y_1(I_m)}{[y_1(I_2)]^{f_2}[y_1(I_3)]^{f_3}}\right) \qquad (12)$$

Under the condition that $y_1(I_2) = y_1(I_3) = y_1$, which includes the requirement of ideality, namely $y_1(I_2) = y_1(I_3) = 1$, and from (6), (7), (9) and (10) we have:

$$C'_2/M_2 = C'_3/M_3 \qquad (13)$$

and

$$\mu_1^E = RT \ln[y_1(I_m)/y_1] \qquad (14)$$

If, in addition, isotonic mixing is also ideal, i.e. $y_1(I_m) = 1$, or even if $y_1 = y_1(I_m)$, then:

$$\mu_1^E = 0 \qquad (15)$$

Corresponding to the excess isotonic chemical potential, the excess osmotic pressure Π^E is given by:

$$\Pi^E V_1 = -\mu_1^E \qquad (16)$$

where V_1 is partial molar volume of the solvent, and this clearly shows that zero isotonic excess indicates ideality, i.e. the equality of the activity coefficients $y_1(I_2)$, $y_1(I_3)$ and $y_1(I_m)$; and a non-zero excess represents a departure from ideality.

Isotonic excess in terms of virial coefficients

Further insight into the nature of the excess osmotic pressure may be obtained from the statistical mechanical theory of McMillan and Mayer[4], which is primarily a theory of imperfect gases. This theory leads to an expansion of pressure in powers of volume or concentration, and also establishes the legitimacy of the intuitive notion that the osmotic pressure of a liquid solution can be treated as the pressure of a gas. Consequently, and at low concentrations, the osmotic pressure of a binary solution can be approximated to:

$$\Pi = RTC_i/M_i + \tfrac{1}{2}a_{ii}C_i^2 \tag{17}$$

which, for the isotonic solutions I_2 and I_3, becomes:

$$\Pi_2 = RTC'_2/M_2 + \tfrac{1}{2}a_{22}C'^2_2 \tag{18}$$

$$\Pi_3 = RTC'_3/M_3 + \tfrac{1}{2}a_{33}C'^2_3 \tag{19}$$

Also, the osmotic pressure of the ternary isotonic mixture I_m takes the form:

$$\begin{aligned}\Pi_m = RT(&f_2C'_2/M_2 + \tfrac{1}{2}a_{22}f_2^2C'^2_2/M_2^2 + \tfrac{1}{2}a_{33}f_3^2C'^2_3/\mathrm{M}_3^2\\ &+ a_{23}f_2f_3C'_2C'_3/M_2M_3)\end{aligned} \tag{20}$$

assuming that $a_{23} = a_{32}$. Now, since:

$$\Pi = \Pi_2 = \Pi_3 = f_2\Pi_2 = f_3\Pi_3$$

$$\Pi^E = \Pi_m - \Pi = \Pi_m - f_2\Pi_2 - f_3\Pi_3 \tag{21}$$

we have, from equations (18), (19), (20) and (21):

$$\begin{aligned}\Pi^E = RTf_2f_3(&a_{23}C'_2C'_3/M_2M_3 - \tfrac{1}{2}a_{22}C'^2_2/M_2^2\\ &- \tfrac{1}{2}a_{22}C'^2_2/M_2^2)\end{aligned} \tag{22}$$

The expression within brackets in equation (22) formally resembles polymer–polymer interaction terms obtained by others[1–3,5] for thermodynamic functions other than excess osmotic pressure. Giving this expression the symbol β_{23}, we may write:

$$\Pi^E = RTf_2f_3\beta_{23} \tag{23}$$

From equation (23), it is easily seen that Π^E has a maximum at $f_2 = f_3 = 0.5$ for positive values of the interaction parameter β_{23}, which is concentration-dependent. Therefore:

$$\beta_{23} = 4\Pi^E_{max}/RT \tag{24}$$

A direct evaluation of 2–3 interaction by using the above equation should be interesting, since, as Scott[2] pointed out, this cannot be done by ordinary osmometric methods.

Although this paper deals with osmotic pressure, changes in other thermodynamic properties such as enthalpy and volume, associated with isotonic mixing, will give important information.

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APPENDIX

I_2, I_3	isotonic solutions of polymer 2 and polymer 3, respectively, in the same solvent
I_m	a mixture of I_2 and I_3
C'_2	g of polymer 2 in 1 ml solvent in I_2
C'_3	g of polymer 3 in 1 ml solvent in I_3
C	g of polymer in 1 ml solvent in a general case
$x_1(s)$	mole fraction of solvent in solution *s*
$y_1(s)$	activity coefficient of solvent in solution *s*
Π	osmotic pressure of I_2 or I_3
Π_m	osmotic pressure of I_m
Π^E	excess osmotic pressure $= \Pi_m - \Pi$
Π_2, Π_3	osmotic pressures of I_2, I_3
$\mu_1(s)$	chemical potential of solvent in solution *s*