[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF CORNELL UNIVERSITY]

Phase Equilibria in Polymer–Solvent Systems[1,2]

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Phase equilibria have been investigated in diisobutyl ketone–polyisobutylene and in cyclohexane–polystyrene systems, using carefully fractionated samples so selected as to cover wide ranges in molecular weight ($M \times 10^{-4} = 2.27$, 28.5 and 600 for polyisobutylene; 4.36, 8.9, 25.0 and 127 for polystyrene). The temperature–composition equilibrium curves, though similar in character to those calculated from the thermodynamic theory of polymer solutions, are broader and the critical volume fractions v_2 are approximately twice those predicted by the theoretical relationship $v_2(\text{crit.}) \cong x^{-1/2}$ where x is the ratio of the molar volumes of polymer and solvent molecules. The reciprocal of the critical consolute temperature T_c increases linearly with $1/x^{1/2} + 1/2x$ in strict accordance with theory. The thermodynamic parameters calculated from the slopes and intercepts are at variance with those deduced by other methods, however. Thus, the critical temperature depends on molecular weight in the manner predicted by theory, but the values of the parameters deduced from this dependence appear to be unacceptable. Phase diagrams for the three-component system consisting of cyclohexane and two polystyrenes ($M \times 10^{-4} = 8.9$ and 127, respectively), investigated at 25.5° and 28.2°, exhibit deviations which appear to be related to those for the two-component systems. However, the ratios of the two polymer components at the plait points at each of these temperatures and the dependence of the maximum precipitation temperatures for a fixed ratio of the two polymer components on this ratio agree satisfactorily with theoretical predictions.

Introduction

Liquid–liquid phase separation in high polymer solutions ordinarily occurs with the formation of a highly swollen precipitate.[3,4] This precipitate usually contains many times more solvent than polymer; thus a state of equilibrium is reached between an extremely dilute phase (the supernatant phase) and a moderately dilute phase (the precipitated phase). The temperature–composition phase equilibrium diagram is highly unsymmetrical, the critical composition at incipient incomplete miscibility occurring at a comparatively low concentration of polymer. These characteristics of the phase equilibria obviously have an important bearing on polymer fractionation procedures involving a generally inefficient selective precipitation of species of higher molecular weight. At equilibrium each species is partitioned between the precipitated and supernatant phases.

The theory of polymer solutions developed some years ago[5,6] predicts a high degree of dissymmetry in the phase equilibrium diagram which, qualitatively at least, is in accord with the observations cited above. Quantitative expressions have been derived[5,6] for the consolute temperature and the critical composition, both being given as functions of the molecular weight, and methods for computing the compositions of phases in equilibrium have been set forth. The theory was later extended to molecularly heterogeneous polymers, and some aspects of fractional precipitation were clarified.[7,8]

The present study of phase relations in polymer–solvent systems was undertaken for the purpose of exploring the extent to which reliance may be placed on these theoretical relations from a quantitative point of view. Two non-polar polymers, polyisobutylene and polystyrene, were chosen with the object of minimizing the likelihood of the usually suspected peculiarities attributed to specific interactions. Pure solvents rather than mixtures consisting of a solvent and a precipitant[9,10] were used in order to avoid the complications of treating a three-component system requiring for its description three pair interaction parameters. Diisobutyl ketone was selected for polyisobutylene and cyclohexane for polystyrene because they yield phase separations at convenient temperatures and their refractive indices differ sufficiently from those of the respective polymers to facilitate observation of the phase separation. Carefully prepared polymer fractions were used in order to justify treatment of the mixtures with solvent as two-component systems. The three-component system consisting of mixtures of two polystyrene fractions with cyclohexane provided a simplified prototype of a heterogeneous polymer.

Experimental

Materials.—Three fractions[11] of polyisobutylene were obtained from benzene solutions at 30° by successive additions of acetone. Initial polymer concentrations were about 0.5 g./100 ml., except in the case of the lowest molecular weight fraction where a concentration of 2.5 g./100 ml. was used. The fractions were washed with precipitant and dried *in vacuo* at 60°. The molecular weights of the fractions, designated PBA, PBB and PBC, determined from their intrinsic viscosities in diisobutylene at 20° using the relationship[13] $\log M = (\log [\eta] + 3.444)/0.64$, were 22,700, 285,000 and $\sim$ 6,000,000, respectively.

The polystyrenes were prepared by benzoyl peroxide-catalyzed bulk polymerizations of the undiluted monomer at 60°. The average molecular weights of the parent polymers were controlled by variation of the catalyst concentration, except in the preparation of the lowest molecular weight sample where dodecyl mercaptan was used as a transfer agent. One fraction near the center of the molecular weight distribution of each parent polymer was selected for use. The fractionations were carried out by fractionally precipitating from methyl ethyl ketone solu-

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(1) A portion of this investigation was carried out in connection with the Government Research Program on Synthetic Rubber under contract with the Synthetic Rubber Division, Reconstruction Finance Corporation.

(2) Presented in part before the High Polymer Forum at the Chicago Meeting of the American Chemical Society, Sept. 4, 1950.

(3) J. N. Brönsted and K. Volqvartz, *Trans. Faraday Soc.*, **35**, 576 (1939).

(4) R. B. Richards, *ibid.*, **42**, 10, 20 (1946).

(5) P. J. Flory, *J. Chem. Phys.*, **9**, 660 (1941); **10**, 51 (1942).

(6) M. L. Huggins, *ibid.*, **9**, 440 (1941); *Ann. N. Y. Acad. Sci.*, **43**, 1 (1942); *J. Phys. Chem.*, **46**, 151 (1942); THIS JOURNAL, **64**, 1712 (1942).

(7) P. J. Flory, *J. Chem. Phys.*, **12**, 125 (1944).

(8) R. L. Scott, *ibid.*, **13**, 172, 178 (1945).

(9) J. N. Brönsted and K. Volqvartz, *Trans. Faraday Soc.*, **36**, 61 (1940).

(10) P. O. Powers, *Ind. Eng. Chem.*, **41**, 126 (1949); **42**, 2558 (1950).

(11) PBA and PBB, previously designated as PB5F4 and PB4F3, respectively, have been described[12] as to source and fractionation procedure.

(12) T. G. Fox, Jr., and P. J. Flory, THIS JOURNAL, **70**, 2384 (1948).

(13) P. J. Flory, *ibid.*, **65**, 372 (1943).

tions at 30° with successive additions of methanol.[12] Initial polymer concentrations and subsequent treatment of fractions were identical with those of the polyisobutylene fractionations. The molecular weights of the fractions PSA, PSB, PSC and PSD as determined from their intrinsic viscosities in benzene solution at 30° using the relationship[14] $\log M = (\log [\eta] + 4.013)/0.74$ were 43,600, 89,000, 250,000 and 1,270,000, respectively.

The solvents, diisobutyl ketone and cyclohexane, were of high purity. They were dried over $MgSO_4$ and freshly distilled before use.

Determination of Phase Separation.—Preliminary work on the polyisobutylene (PBB)–diisobutyl ketone system was carried out using a photoelectric turbidimeter[15] consisting of a mercury vapor lamp, monochromatic filter, collimating lenses, solution cell, photoelectric cell and photovolt meter. The operation of this apparatus was cumbersome, and an excessive volume (10 ml.) of solution was required; protection from atmospheric moisture, proper temperature control and provision of adequate stirring of more viscous solutions presented further difficulties. Substitution of visual observation for the photoelectric device permitted the design of a much simpler apparatus in which the above difficulties were minimized. Furthermore, the precipitation points could be observed visually with less ambiguity and with a precision at least as good as by the more elaborate photoelectric method. All data reported here were obtained by the visual method described below.

Measurements on the polyisobutylene–diisobutyl ketone system were conducted using a cell consisting of a 10 × 75-mm. test-tube fitted by means of a rubber tubing jacket to a glass column 7 cm. in length having a short side-arm connecting to a small desiccant (Drierite) bulb. Solvent vapor permeation of the rubber connector was troublesome, but not intolerably so. A rotary glass stirrer, equipped with three tight-fitting "Teflon" washers, was inserted through the column and to the bottom of the test-tube. The washers functioned as bearings for the stirrer and as baffles to vapor diffusion. The column top and stirrer were fitted with rubber tubes which sealed the system when stirring was stopped. The simplicity of these set-ups permitted operation of a number of them simultaneously.

The polyisobutylene sample and solvent were weighed into the apparatus, allowed to stand (capped) a few degrees above the precipitation temperature until the polymer was highly swollen and then stirred to complete the solution. Concentrations were calculated at 30° disregarding possible volume change on mixing. 1.253 was used as the specific volume of diisobutyl ketone and the relation $\bar{v} = 1.097 + 32/M$ was used for the specific volumes of the polyisobutylenes at 30°.[16] Precipitation was effected by allowing the solutions to cool slowly while immersed in a well-stirred bath (oil or water), which provided heat lagging. Temperatures were measured with calibrated thermometers graduated to 0.1° immersed in the bath. Side lighting and a graduated scale placed behind the solution tubes facilitated the detection of the incidence of phase separation, which is manifested by a blurring in the appearance of the lines of the scale.

Taper-jointed tubes and drying columns were used for the polystyrene–cyclohexane system (Fig. 1). These resembled the tubes described above except for the replacement of the tube-to-column rubber connectors with ground glass joints, glass closure of the drying column at a height sufficient to contain the rotary glass stirrer, and the elimination of the "Teflon" washers. A 3-cm. glass tube was used to replace the drying column during the brief stirring operations and served as a close-fitting shank for the glass stirrer.

In preparing a polystyrene solution the drying column was detached and stoppered, the tube, stirrer and a ground glass cap were weighed, and the solution components were then weighed into the tube. Having weighed the all-glass apparatus (drying column replaced by weighing cap) and solution, it was possible by reweighing to know precisely at any time the polymer concentration by deducting the amount of solvent lost by evaporation into the drying column and through the ground glass joint. A given initial solution was thus run at progressively higher polymer concentrations attained by solvent evaporation. Agreement between precipitation temperatures, T_p, of solutions which had undergone considerable (up to 70%) solvent loss and new solutions having the final concentrations attained by the former demonstrated the validity of the technique. The volume fractions, v_2, of polystyrene in the solutions were calculated at 20° using as the specific volumes of the polystyrene and cyclohexane 0.924_0[17] and 1.283_7, respectively, disregarding possible volume changes during mixing.[18] The solutions were thoroughly stirred immediately before and weighed immediately after the precipitation determinations. Precipitation was effected and observed as described above.

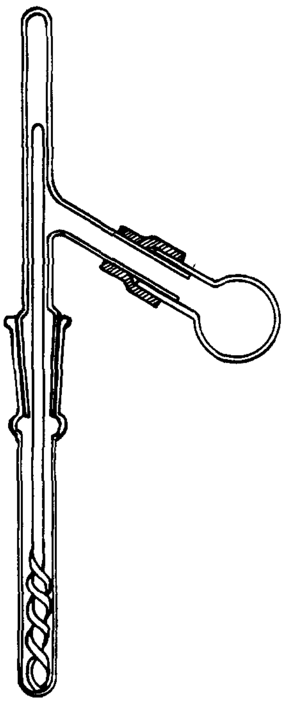

Fig. 1.—Precipitation apparatus.

Precipitation temperatures, T_p, of the polymer solutions were ascertained to ±0.1° except in solutions of polymer volume fraction, v_2, less than 0.01 in which instances heterogeneity of the fractions caused an uncertainty of ±0.2 to ±0.4° in some cases; this effect was greatest with the lower fractions. The highest molecular weight fractions presented the further problem of some macroscopic solution non-homogeneity arising from solvent reflux in the more concentrated solutions where adequate stirring was difficult. The rate of cooling between 0.01 and 0.05° per minute was not critical. Reversibility of the phase separation was possible with slow temperature increase, and phase coalescence occurred at the same T_p, observed with decreasing temperature provided that the system had not been allowed to cool more than a few tenths of a degree below T_p. The same precipitation temperature was observed with and without stirring.

In order to investigate phase equilibria in a ternary system of two polymer fractions and a solvent, four weighed mixtures of fractions PSB and PSD were dissolved in small volumes of distilled benzene, the solutions were stirred thoroughly and the polymer mixtures were precipitated with methanol. Care was taken to effect the precipitation rapidly in small amounts of solvent; negligible loss of polymer was then assured. The powdery mixtures were washed with small amounts of methanol and dried *in vacuo* at 60° for four hours. Cyclohexane solutions of these mixtures were prepared and T_p determinations identical with those employed for individual polystyrene fractions were performed.

Solutions of the mixed fractions in cyclohexane were prepared having compositions within the two-phase regions of chosen isothermals (25.5 and 28.2°) in order to determine tie-lines. Tubes similar to those described above, but having 10-ml. capacity, were used. The solutions were slowly cooled with constant stirring to the temperature being investigated. The two-phase mixtures were thermostated at this temperature and stirred for an additional 20 minutes. The phase more concentrated in polymer in each tube was allowed to settle and a portion of the clear supernatant phase was quickly transferred to a weighing bottle by means of a pipet the temperature of which was approximately 10° above that of the mixture. The concentration of polymer in the supernatant phase was obtained by first weighing the sample of solution removed, then evaporating to dryness and weighing the polymer residue.

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[14] R. H. Ewart, paper presented at the Atlantic City Meeting of the American Chemical Society, April 14, 1947.

[15] G. Gavoret and M. Magat, *J. chim. phys.*, **46**, 355 (1949).

[16] T. G. Fox, Jr., and P. J. Flory, *J. Phys. Colloid Chem.*, **55**, 221 (1951).

[17] T. G. Fox, Jr., and P. J. Flory, *J. Applied Phys.*, **21**, 581 (1950).

[18] W. Heller and A. C. Thompson, *J. Coll. Sci.*, **6**, 57 (1951).

Results and Discussion

Phase Equilibria in Two-component Systems.—The statistical thermodynamic theory of polymer solutions[5,6] expresses the chemical potential of the solvent in a solution composed of a low molecular weight solvent and a polymer homogeneous in molecular weight as

$$\mu_1 - \mu_1^0 = RT\,[\ln(1 - v_2) + (1 - 1/x)v_2 + \chi_1 v_2^2] \quad (1)$$

where v_2 is the volume fraction of polymer in the solution. x is the number of segments per polymer chain and is equal to the ratio of the molar volume of the polymer to that of the solvent. The thermodynamic interaction parameter χ_1 is composed of a temperature independent entropy parameter and a temperature dependent energy parameter. In recent notation[19,20]

$$\chi_1 = \frac{1}{2} - (\psi_1 - \kappa_1) \quad (2)$$

where ψ_1 is the entropy parameter and κ_1 is the energy parameter, the latter being inversely proportional to the absolute temperature. Further, κ_1 and ψ_1 are related in the manner

$$\kappa_1/\psi_1 = \Theta/T \quad (3)$$

where T is the absolute temperature and Θ is the incipient immiscibility temperature for molecules of infinite molecular weight.

While relationships of the form of equation (1) have been shown to be generally inappropriate in dilute solutions, owing to the non-random distribution of polymer segments at high dilution[21-24] deviations from them should vanish as the temperature Θ is approached. As the phase equilibria studies for polymers of high molecular weight must necessarily be conducted at temperatures very close to Θ, objections to equation (1) which normally apply for dilute solutions are of no consequence here. At temperatures near $T = \Theta$ the "excluded volume" of a polymer molecule in dilute solution is very small, being zero at Θ. The polymer molecules then telescope one another freely and all polymer segments, including those occurring (momentarily) within the interior of the random coils, are not subject to shielding by the external segments. Hence, the basic premise on which equation (1) is derived, namely, that all regions of space are equally available to a given molecule, may be considered to apply.

The critical concentration and interaction parameter for incipient phase separation for a solution containing a single polymer species obtained by equating to zero the first and second derivatives of the chemical potential with respect to the concentration are[5]

$$(v_2)_c = 1/(1 + x^{1/2}) \quad (4)$$

$$(\chi_1)_c = (1 + x^{1/2})^2/2x \quad (5)$$

Substitution of relations (2) and (3) into equation (5) yields

$$1/T_c = (1/\Theta)[1 + (1/\psi_1)(1/x^{1/2} + 1/2x)] \quad (6)$$

Figures 2 and 3 represent the results of the precipitation determinations for polyisobutylene–diisobutyl ketone and polystyrene–cyclohexane solutions, respectively. Plotting the reciprocals of the critical precipitation temperatures, $1/T_c$, observed for the polymer fractions against $(1/x^{1/2} + 1/2x)$ as in Fig. 4 gives a straight line as predicted by

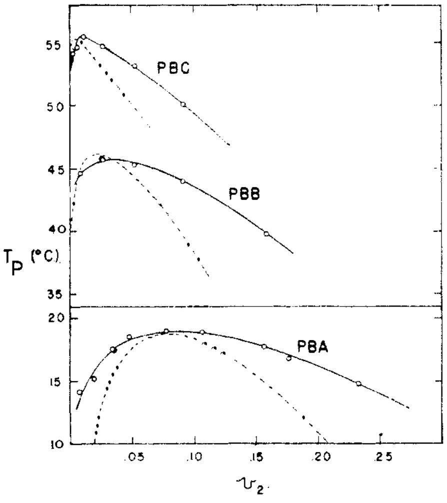

Fig. 2.—Precipitation temperatures T_p for polyisobutylene fractions in diisobutyl ketone plotted against concentration expressed as volume fractions v_2 of polymer. The broken lines are the corresponding theoretical curves.

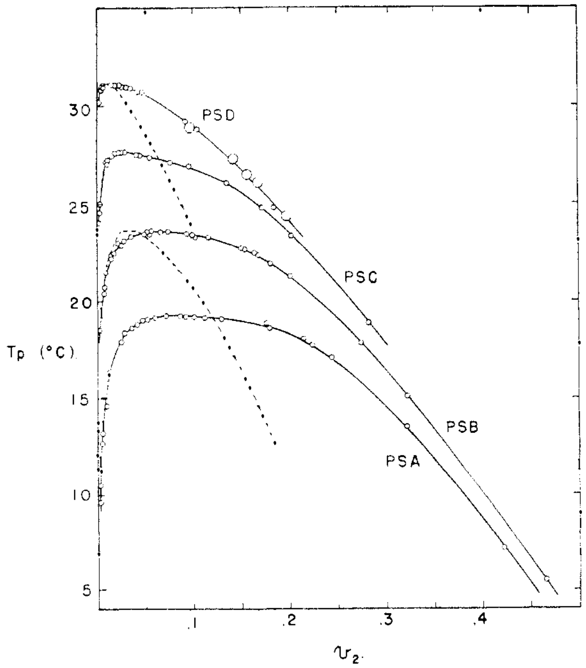

Fig. 3.—Precipitation temperatures T_p for polystyrene fractions in cyclohexane plotted against polymer volume fractions v_2. Theoretical curves are shown for two of the fractions.

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[19] "Annual Review of Physical Chemistry," Vol. II, Annual Reviews, Inc., Stanford, California, 1951, p. 383 ff.

[20] Our χ_1 is the equivalent of the μ_1 (or μ) widely used in the polymer literature. We prefer the former in order that the symbol μ may be reserved for the chemical potential.

[21] P. J. Flory, *J. Chem. Phys.*, **13**, 453 (1945); **17**, 303 (1949); **17**, 1347 (1949).

[22] T. G. Fox, Jr., and P. J. Flory, *J. Phys. Colloid Sci.*, **53**, 197 (1949).

[23] P. J. Flory and W. R. Krigbaum, *J. Chem. Phys.*, **18**, 1086 (1950).

[24] P. J. Flory and T. G. Fox, Jr., This Journal, **73**, 1904 (1951).

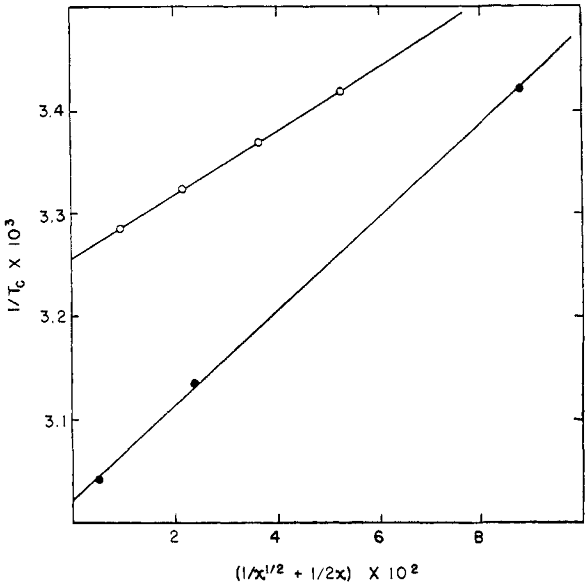

Fig. 4.—Reciprocal critical precipitation temperatures $1/T_c$ plotted against $(1/x^{1/2} + 1/2x)$ for various polystyrene fractions in cyclohexane (open circles) and polyisobutylene fractions in diisobutyl ketone (solid circles).

equation (6). Θ and ψ_1 values obtained from the intercepts and slopes of the plots are 331.1°K. and 0.6534, respectively, for the system polyisobutylene–diisobutyl ketone and 307.2°K. and 1.0558, respectively, for the system polystyrene–cyclohexane.

Agreement of experimental data with the form of equation (6) appears to be general for polymer–solvent systems exhibiting phase separation.[25-29] Figure 5 represents the critical precipitation data of Jenckel and Heinen[25] for the system: fractionated polystyrene–octadecanol. The molecular weights used in the figure are those given in the publication cited; the critical precipitation temperatures were obtained by reading the temperatures corresponding to the peaks of the precipitation curves as drawn in that publication. The straight line shown in Fig. 5 was fitted to the series of precipitation data (open circles) exhibiting the least scatter. The values thus obtained for ψ_1 and Θ are 1.3 and 475°K., respectively.

Substitution of ψ_1 and Θ values into (2), which has the form

$$\chi_1 = \frac{1}{2} - \psi_1 + \psi_1\Theta/T \qquad (2a)$$

gives numerical correlation of the theoretical parameter χ_1 and the absolute temperature for each system. This procedure represents, in effect, a calibration of the χ_1 scale in terms of temperature through the use of the indicated theoretical expressions and experimentally observed critical miscibility temperatures.

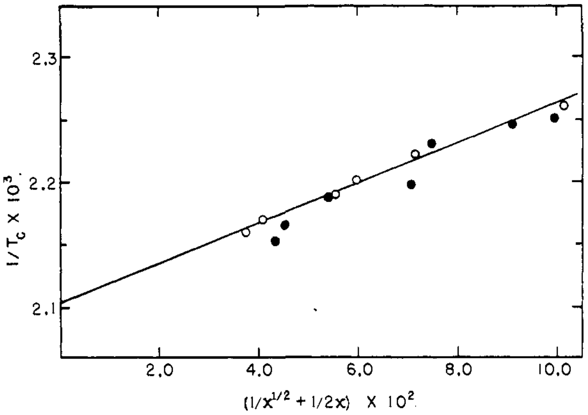

Fig. 5.—Reciprocal critical precipitation temperatures $1/T_c$ plotted against $(1/x^{1/2} + 1/2x)$ for various polystyrene fractions in octadecanol from the data of Jenckel and Heinen.[25] Open and solid circles represent two different series of measurements.

Having performed the above calibration, it is now possible to compare observed phase equilibria curves with those predicted by statistical thermodynamic theory. The compositions of the two phases in equilibrium, expressed as the volume fractions v_2 and $v_2'(v_2 < v_2')$ of polymer, are given by the following expression derived[7] from equation (1) and the corresponding expression for the chemical potential of the solute in a two-component system consisting of a single polymer species of size x and a solvent.

$$v_2 = \{-(\gamma + 1)g + [(\gamma + 1)^2g^2 + 4(\gamma - 1)^3g]^{1/2}\}/2(\gamma - 1)^3 \qquad (7)$$

where γ and g are convenient variables for simplifying the calculation defined by

$$\gamma \equiv v_2'/v_2$$
$$g = (12/x)[(\gamma + 1)(\ln \gamma)/2 - (\gamma - 1)]$$

By choosing values for γ, pairs of volume fractions v_2 and v_2' are obtained for each polymer homolog. The value of χ_1 corresponding to each γ, v_2 pair may be calculated from the equation[7]

$$\chi_1 = \frac{(1/x) \ln \gamma + v_2(1 - 1/x)(\gamma - 1)}{v_2(\gamma - 1)[2 - v_2(\gamma + 1)]} \qquad (8)$$

Using also the conversion of χ_1 to T by (2a), three theoretical T_p *vs.* v_2 curves calculated in this manner have been drawn for the polyisobutylene–diisobutyl ketone system, Fig. 2, and two such curves were constructed for the polystyrene–cyclohexane system, Fig. 3. The shapes of the calculated curves agree only qualitatively with those observed. The latter are markedly broader and the observed critical points occur at higher polymer concentrations than those predicted (see equation (4)). The latter feature is more marked in the polystyrene–cyclohexane system. Divergence from theory is similar nevertheless in both systems studied. This divergence indicates that the primary theoretical equation (1) is somewhat inaccurate in its representation of the dependence of the chemical potential on concentration.

An even more disturbing feature occurs in the values obtained for the entropy of dilution parameter ψ_1. Analysis of all studies of critical misci-

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(25) E. Jenckel and I. Heinen, *Z. Naturforsch.*, **5a**, 317 (1950).

(26) T. G. Fox, Jr., and P. J. Flory, THIS JOURNAL, **73**, 1909 (1951); **73**, 1915 (1951).

(27) H. L. Wagner and P. J. Flory, *ibid.*, **74**, 195 (1952).

(28) L. Mandelkern and P. J. Flory, *ibid.*, **74**, 2517 (1952).

(29) P. J. Flory, L. Mandelkern, J. B. Kinsinger and W. B. Shultz, *ibid.*, **74**, 3364 (1952).

bility as a function of molecular weight as reported in recent papers from this Laboratory[26-29] yield ψ_1 values exceeding 0.5, whereas according to intrinsic viscosity measurements ψ_1 seldom exceeds 0.10; similar magnitudes (0.10) are indicated by osmotic studies in those instances in which adequate measurements have been made at a series of temperatures. Solvents consisting of cyclic molecules yield higher ψ_1 values than acyclic ones, according to the viscosity studies. The preceding analysis of critical miscibility results for the two systems cyclohexane–polystyrene and octadecanol–polystyrene place the ψ_1's in opposite order. It is to be noted, however, that the viscometric and osmotic results refer to higher dilutions than those involved at critical miscibility, which again indicates failure of the theory to represent accurately the concentration dependence. Since the chemical potential is resolved into its entropy and energy components through the operation of differentiation with respect to temperature, the disparity between values obtained for ψ_1 (and for κ_1 as well) by different methods shows that the deviation from equation (1) must change with temperature.

Phase Equilibria in a Three-component System. —The compositions of the polymer fraction mixtures prepared as described above for use in the study of phase equilibria of a ternary system are listed in Table I. v^0_{PSB} is the volume fraction of PSB in each mixture. The number-, weight- and z-average number of segments, $\bar{x}_n$, $\bar{x}_w$ and $\bar{x}_z$, were calculated assuming fractions PSB and PSD to be monodisperse polymer homologs having 768 and 10,950 segments per molecule, respectively.

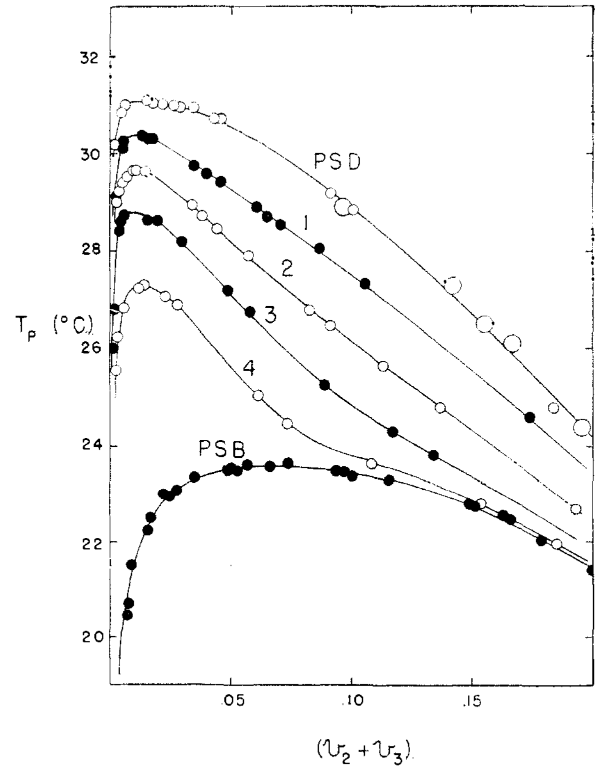

Fig. 6.—Precipitation temperatures T_P plotted against total volume fractions of polymer ($v_2 + v_3$) for the mixed polystyrene fractions (PSB + PSD)-cyclohexane system (see Table I for the polymer mixture compositions).

TABLE I

Mixture	v^0_{PSB}	$\bar{x}_n$	$\bar{x}_w$	$\bar{x}_z$	T_{PT} (°C.)
PSD	0.000	10,950	..	....	31.1
1	.500	1,432	5859	10,283	30.4
2	.750	1,002	3314	9,180	29.6
3	.900	854	1786	7,010	28.8
4	.980	781	968	3,027	27.3
PSB	1.000	768	..	....	23.6

Figure 6 presents the precipitation data obtained for these mixtures in cyclohexane plotted as the precipitation temperature against the total polymer volume fraction.

The triaxial phase diagrams, Figs. 7 and 8, for the three-component system at 25.5 and 28.2°, respectively, have been constructed from the curves shown in Fig. 6. All solutions of a mixture of two polymer fractions present in a fixed ratio to one another lie in the triaxial diagram on a single straight line passing from the pure solvent vertex

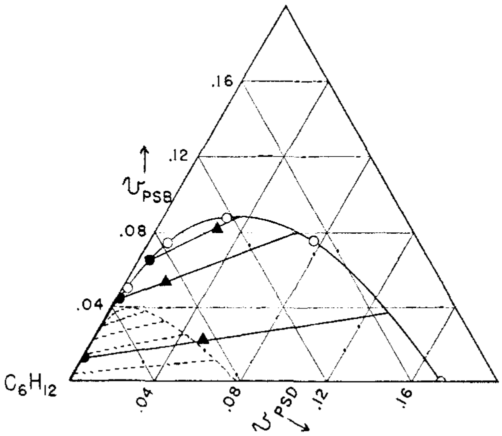

Fig. 7.—Experimental and theoretical (broken lines) phase equilibria diagrams for the system PSB–PSD–cyclohexane at 25.5°.

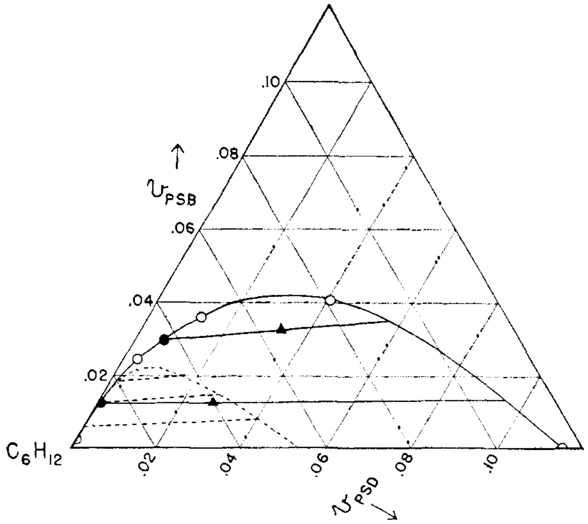

Fig. 8.—Experimental and theoretical (broken lines) phase equilibria diagrams for the system PSB–PSD–cyclohexane at 28.2°.

and cutting the opposite (PSB–PSD) base line into the proportions of the undiluted polymer mixture. To construct an isothermal phase equilibria curve for the cyclohexane (1)–PSB(2)–PSD(3) system, and isothermal line was struck through the T_p *vs.* $(v_2 + v_3)$ curves of Fig. 6. The $(v_2 + v_3)$ values corresponding to precipitation for each mixture–solvent system at the chosen temperature were noted and these values have been plotted on the corresponding mixture ratio lines described above. A smooth curve drawn through the points so plotted is the isothermal for the temperature selected. The gross compositions (actually points of unattainable concentration at the temperature being investigated) of the solutions prepared for the tie-line determinations are indicated by solid triangles in the two-phase regions of Figs. 7 and 8. The experimentally observed dilute solution end points of the tie-lines through these gross compositions are shown as solid circles. These two points determine the tie-line.

The statistical thermodynamic expression for the chemical potential in a system consisting of more than one polymer species[7,8] has been applied by Tompa[30] and Scott[31] to the problem of phase equilibria in a three-component system. In a system consisting of a solvent (1) and two polymer fractions (2 and 3) the thermodynamic interaction parameter χ_{23} between the polymer homologs is zero and the other pairs yield identical parameters $\chi_{12} = \chi_{13} = \chi_1$. Adopting Tompa's formulation, an isothermal (χ_1 constant) for such a three-component system may be calculated as follows. Defining the total volume fractions of polymer in two phases in equilibrium as $v = v_2 + v_3$ and $v' = v_2' + v_3'$, $v' > v$, and defining the ratios of the concentrations of the individual polymer species in the two phases as $\gamma_2 = v_2'/v_2$ and $\gamma_3 = v_3'/v_3$, a parameter α is obtained such that $\ln \gamma_2 = \alpha x_2$ and $\ln \gamma_3 = \alpha x_3$. x_2 and x_3 are the number of segments per chain in polymer species 2 and 3. α is related to the interaction parameter by

$$\alpha = \ln\left(\frac{1 - v'}{1 - v}\right) + 2\chi_1(v' - v) \tag{9}$$

According to the thermodynamic conditions for equilibrium, the function

$$\varphi = \ln\left(\frac{1 - v'}{1 - v}\right) + (v' - v) + \chi_1(v'^2 - v^2) - \left[\frac{(\gamma_2 - 1)(\gamma_3 v - v')}{x_2(\gamma_3 - \gamma_2)} + \frac{(\gamma_3 - 1)(v' - \gamma_2 v)}{x_3(\gamma_3 - \gamma_2)}\right] \tag{10}$$

must vanish when the correct v and v' combination is secured. Solution may be effected by choosing a value for v, guessing v' and calculating a trial α by means of equation (9). γ_2 and γ_3 are then calculated, and the tentative set of values for v, v', γ_2 and γ_3 is substituted into equation (10) to obtain a numerical value for φ. A new trial v' is selected and the process is repeated, etc., until the value of v' which gives $\varphi = 0$ is found. This is conveniently carried out by plotting φ against v'. With the correct v and v' combination and corresponding γ_2 and γ_3 values, the concentrations v_2, v_3, v_2' and v_3' of the polymer homologs in phases in equilibrium at the chosen χ_1 (or corresponding temperature, T) are obtained and a tie-line of the isothermal is established. Other tie-lines are computed in the same way by choosing other values for v.

Theoretical curves computed in the above manner for the cyclohexane–PSB–PSD system are compared with the experimental curves in Figs. 7 and 8. χ_1 values 0.5309 and 0.5204 corresponding to the temperatures 25.5 and 28.2° as calculated by (2a), were used. The experimental curves are seen to possess the form predicted, but as was noted in the two-component system the two-phase regions observed are considerably larger than predicted by theory.

The critical point on a given isothermal, *i.e.*, the point at which the compositions of the conjugate phases become identical, can be located according to theory with the aid of equations developed by Stockmayer.[32] Proceeding from the expressions[7] describing phase equilibria of solutions of a heterogeneous polymer of fixed molecular weight distribution, he found for the critical volume fraction of polymer $(1 - v_1)_c$ and the critical interaction parameter $(\chi_1)_c$

$$(1 - v_1)_c = \frac{1}{1 + \bar{x}_w \bar{x}_z^{1/2}} \tag{11}$$

$$(\chi_1)_c = \frac{(1 + \bar{x}_w^{1/2})^2}{2\bar{x}_w} + \frac{(\bar{x}_z^{1/2} - \bar{x}_w^{1/2})^2}{2\bar{x}_w \bar{x}_z^{1/2}} \tag{12}$$

$\bar{x}_w$ and $\bar{x}_z$ are the weight- and *z*-average number of segments per chain in the heterogeneous polymer.

In view of the rather large divergence of the observed from the theoretical curves of the phase diagrams, both for the two- and the three-component systems of the present study, the observed $(1 - v_1)_c$ cannot be expected to coincide with the predicted $(1 - v_1)_c$. However, it is conceivable that the ratio of $(v_2)_c$ to $(v_3)_c$ may be given satisfactorily by theory. Substituting 0.5309 and 0.5204 for $(\chi_1)_c$ in equation (12), it is found that the theoretically predicted critical points for the 25.5 and 28.2° isothermals should exist at ratios of PSB to PSD of 8.40:1 and 3.22:1, respectively. Although experimental tie-lines were not determined sufficiently near each critical point to definitely fix the location of the critical point, critical ratios of about 7 and 3, respectively, are indicated by the pattern of the tie-lines shown in Figs. 7 and 8. These are slightly lower than those calculated but the differences are less than the experimental uncertainty.

A problem of practical importance is the determination of the highest temperature at which phase separation can occur in a system composed of a single solvent and a heterogeneous polymer of fixed molecular weight distribution. Tompa[33] correctly indicated the difference between this "apparent critical" point, or precipitation threshold temperature, and the true critical point, and carried out a theoretical calculation of this precipitation threshold temperature, T_{PT}. (Actually the corresponding minimum interaction parameter $(\chi_1)_m$ is calculated.) The results of his derivation

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(30) H. Tompa, *Trans. Faraday Soc.*, **45**, 1142 (1949).

(31) R. L. Scott, *J. Chem. Phys.*, **17**, 268 (1949); *ibid.*, **17**, 279 (1949).

(32) W. H. Stockmayer, *ibid.*, **17**, 588 (1949).

(33) H. Tompa, *Trans. Faraday Soc.*, **46**, 970 (1950).

may be formulated in the following equations for purposes of calculation.

$$V \equiv \sum_{i=2}^{n} v_i^0 Y^{x_i} = (1 - v_1')/(1 - v_1) \qquad (13)$$

$$W \equiv \sum_{i=2}^{n} (v_i^0/x_i)(Y^{x_i} - 1) \qquad (14)$$

$$U \equiv (1 - V)/(-W + \ln Y) \qquad (15)$$

$$A \equiv \frac{(2 + UW) + [(2 + UW)^2 - 8U(1 - V + W)]^{1/2}}{4U} = \chi_1(v_1 - v_1') \qquad (16)$$

$$v_1 = (UA - 1)/UA \qquad (17)$$

$$v_1' = 1 - V(1 - v_1) \qquad (18)$$

$$\ln Y = (1/x_i) \ln (v_i'/v_i),\ v_i' > v_i \qquad (19)$$

$$\ln Y = 2A - \ln (v_1/v_1'),\ v_1 > v_1' \qquad (20)$$

$$(\chi_1)_m = A/(v_1 - v_1') \qquad (21)$$

v_1 and v_1' are the volume fractions of solvent in the two phases which separate at the precipitation threshold. v_i and v_i' are the volume fractions of polymer species $i (i > 1)$ in those phases. v_i^0 is the volume fraction of polymer species i in the heterogeneous polymer (*i.e.*, when $v_1 = 0$). x_i is the number of segments per chain of species i. V, W, U, A and Y are convenient variables defined by the above equations. The x_i values of the polymer fractions (considered monodisperse) used in the present study are known and the v_i^0 values are known for each polymer mixture (see Table I).

$(\chi_1)_m$ is calculated for each polymer mixture as follows: A reasonable guess is made for the value of ln Y. (Y should be very slightly greater than unity.) V, W and U are calculated by equations (13), (14) and (15), respectively. A is then computed from equation (16). After obtaining v_1 and v_1' from equations (17) and (18), a value for ln Y is calculated according to equation (20). The correct guess for ln Y would equal the calculated ln Y. By taking successive trial ln Y values and plotting their differences, Δ ln Y, from the calculated values against the trial ln Y, the correct solution for which Δ ln $Y = 0$ may be obtained. The magnitudes of the experimental quantities are such that Δ ln Y values in the neighborhood of the correct ln Y are extremely small. However the passage of Δ ln Y from positive to negative values is rapid enough to define the desired $(\chi_1)_m$, calculated by equation (21), to an accuracy greater than experimentally attainable.

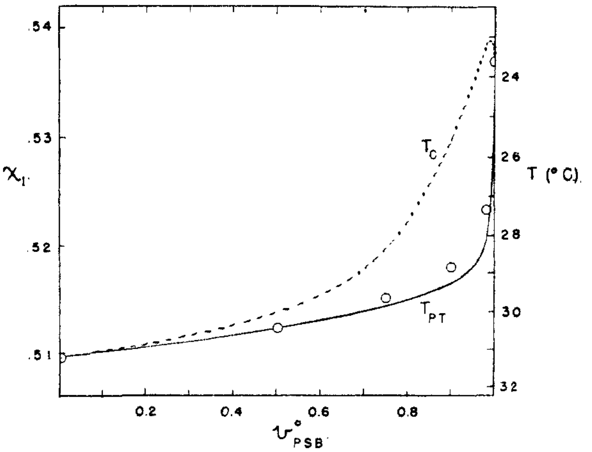

Fig. 9.—Experimental (open circles) and theoretical (solid line) threshold precipitation temperatures T_{PT} (or the corresponding $(\chi_1)_m$) plotted against the volume fractions v^0_{PSB} of PSB in the pure PSB–PSD mixtures for the system PSB–PSD–cyclohexane. The broken line represents the theoretical critical precipitation temperature T_c (or the corresponding $(\chi_1)_c$) as a function of v^0_{PSB} for the same system.

In Fig. 9 the experimental precipitation threshold temperatures T_{PT} of the four polystyrene mixtures are compared with those calculated (solid curve); calculated critical temperatures T_c are represented by the broken line. Again the T and χ_1 scales have been related according to the previous calibration. The experimental threshold precipitation temperatures (see Table I) are taken from Fig. 6. These represent the temperatures of the isothermals which are tangent to the straight lines which may be drawn in the triaxial diagrams to represent the loci of compositions for which the polymer–polymer ratios assume the respective values used. Although exact coincidence between observed and predicted threshold temperatures is not obtained, the extent of agreement is remarkable noting the considerable differences between the predicted and observed solution compositions at these precipitation temperatures. This conformance with theory of the observed T_{PT} in the ternary system is similar to that observed for T_c in the binary system.

The application of equation (5) to heterogeneous polymers by merely inserting an average molecular weight therein is without theoretical justification, but as a simple empirical procedure it could conceivably serve a useful purpose. If "critical temperatures" are calculated by this equation using the number–average molecular weights of the PSB–PSD polymer mixtures a curve with negative curvature and located well above the true T_c *vs.* v^0_{PSB} curve (broken line of Fig. 9) is obtained. A similar calculation based on the weight–average molecular weights of the polymer mixtures yields a curve lying above the experimentally observed T_{PT} and below the T_c curve. Calculation using the z-average molecular weights produces a "T_c" curve lying well below the T_{PT} *vs.* v^0_{PSB} curve of Fig. 9. Thus the experimentally observed T_{PT} lie between the "T_c" curves calculated by equation (5) using $\bar{x}_w$ and $\bar{x}_z$ values. For an empirical guide, therefore, the apparent critical precipitation temperatures of unfractionated polymers or "rough-cut" fractions will give an estimate of an average molecular weight lying between the weight- and z-average molecular weights of the sample. If the sample is not exceptionally heterogeneous a reasonable approximation to the weight–average molecular weight can be made by such a precipitation measurement.

Conclusions

Throughout all consideration of the application of a theoretical free energy of mixing expression to phase equilibria it is necessary to note that the resulting equations are very sensitive to inaccuracies in the representation of its dependence on concentration. The critical phase equilibria conditions are derived from the first and second derivatives of a chemical potential with respect to concentration variables. Reliance upon the critical conditions thus obtained for quantitative results requires a greater faith in the complete applicability of the chosen model than is probably justified.

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A Study of Molten Borates with the Cr(VI)–Cr(III) Indicator

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The Cr(VI)–Cr(III) indicator is applied to binary borate melts at 1200°. The concentrations of the two valences, each below 0.1%, are determined by titration. Their ratio, corrected for the oxygen pressure above the melt, is taken as a measure for the availability of oxygen ions for bond formation. The systems of B_2O_3 with Li_2O, BaO and ZnO show minima of this oxygen ion availability which are correlated to anomalies in some physical properties reported for the corresponding glasses. With K_2O and PbO, no minima are observed.

Several physical properties of binary boric oxide–metal oxide glasses indicate that an increase in metal oxide concentration, starting from pure B_2O_3, first tightens the structure of the glass to loosen it up above metal oxide equivalent fractions of about 0.1.[2,3c] For instance, the "apparent molar refraction" $R_{O^{2-}}$ introduced by Fajans and Kreidl[4] as a measure of the looseness of oxygen bonding shows minima at equivalent fractions of 0.06 to 0.08 in the systems with Na_2O, K_2O and BaO.[3] It seemed worthwhile to see whether the availability of the oxygen ion for bond formation, as measured with an indicator, would exhibit similar features in the molten mixtures at 1200°.

Indicators which have been employed in liquid oxide systems by Weyl,[5a] Dietzel[5b] and Lux[6] are pairs of metal ions like Cr^{6+}–Cr^{3+}. Their equilibrium, at a specified oxygen pressure, is determined by the availability of oxygen ions (the "oxygen ion concentration" in the terminology of Lux and Flood[7]). The range of the indicator can be extended by using different oxygen pressures. The present view of molten oxides[8] does not permit the assignment of definite formulas to the indicator ions. Formally, their equilibrium can be written as

$$\mathrm{Cr(VI)\ (in\ melt)} \leftrightarrows \mathrm{Cr(III)\ (in\ melt)} + {}^3/_4O_2 \quad (1)$$

In order to compare the results measured at different oxygen pressures, a quantity K' is defined

$$K' = \frac{c_6}{c_3} \times p_{O_2}{}^{-3/4} \quad (2)$$

c_6, c_3 and p_{O_2} denoting the concentration of hexa- and trivalent chromium found by analysis (in weight %) and the partial pressure of oxygen in atmospheres, respectively. This K' is primarily a function of the pseudo-binary oxide composition. All its factors are measured; thus log K' is the analog of Hammett's H-function[9] in protic solvents. The composition of the pseudo-binary borate systems is expressed in this paper by the equivalent fraction of the metal oxide

$$q_{MeO} = 2n_{MeO}/(6n_{B_2O_3} + 2n_{MeO})$$

Me denoting K_2, Ba, etc., n the oxide mol number.

The indicator equilibrium was to be followed by chemical analysis. Therefore the Cr(VI)–Cr(III) pair was chosen. Its hexa- and trivalent ions are fairly stable in aqueous solution and can be titrated without special precautions; also, one would expect only these two valences under the oxygen pressures applied.[10] As to the second component to be added to boric oxide, all oxides occurring in several valences were ruled out by the analytical method used for the indicator. Evaporation from the melt and narrow homogeneous liquidus ranges[11] were other limitations. To have cations of different charge, size and polarizability, the oxides of Li, K, Ba and Zn were chosen, and PbO which permits investigation over the whole concentration range.

Experimental

The general procedure was as follows: A mixture of boric oxide and the corresponding metal oxide containing about 0.1% Cr was held at 1200° in an oxygen–nitrogen atmosphere of known composition until equilibrium was reached. The sample was then quenched and analyzed for the metal oxide and for hexa- and trivalent chromium. By choosing the proper gas atmosphere, the c_6/c_3 ratio was kept between 0.1 and 10 which is convenient for the analysis.

The reagents were boric acid, the nitrates of lithium, potassium and barium, and zinc and lead(II) oxide, all of analytical grade. Chromium was added as $K_2Cr_2O_7$. These components were premelted under either hydrogen or oxygen, checked for the absence of nitrate and then placed into a small 1-ml. platinum crucible. Two of these were hung together into a vertical ceramic tube of 1¼″ i.d.

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(10) However, for CrF_4 and $CrCl_4$ *cf.* H. v. Wartenberg, *Z. anorg. Chem.*, **247**, 135 (1941); **249**, 100 (1942); **250**, 122 (1942).

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