glutathione are denoted by the indices R and G, respectively.

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MINNEAPOLIS, MINNESOTA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF CORNELL UNIVERSITY]

Phase Equilibria in Polymer–Solvent Systems. III. Three-component Systems[1]

BY A. R. SHULTZ AND P. J. FLORY

RECEIVED JULY 20, 1953

Phase equilibria data for three ternary solvent–solvent–polystyrene systems have been obtained and interpreted in terms of the statistical–thermodynamic theory of polymer solutions. Thermodynamic interaction parameters calculated from the observed plait points are consistent with those calculated for solvent–solvent and solvent–polymer pairs from binary system liquid–vapor and liquid–liquid phase equilibria data.

Introduction

Investigations on liquid–liquid phase equilibria in binary systems consisting of a polymer and a single solvent have yielded results which on the whole agree rather well with the predictions of the statistical–thermodynamic theory of polymer solutions.[2] Although the theory succeeds only qualitatively in reproducing the observed binodials, the critical miscibility temperatures T_c vary with molecular weight in the manner predicted by the theory.[3] The polymer–solvent interaction parameters calculated from this dependence of T_c on the molecular weights of polymer fractions are remarkably similar to those of chemically analogous small molecule liquid pairs.[4] This correlation of the thermodynamic functions of large and small molecules is important in providing a common thermodynamic basis for comparing polymers with possibly better characterized small molecule liquids. It may thus be possible to study with greater facility the properties of polymers which are actually peculiar to their great size and chain structure.

The practical use of solvent–non-solvent mixtures to effect separation of polymers into less heterogeneous fractions has been reviewed by Cragg and Hammerschlag.[5] Powers[6] has made several phase studies on polystyrene–mixed solvent systems. Polymer solution theory has been extended to ternary and more complex systems to explain and predict various phenomena dependent upon the free energies of the components.[7–9]

It is the purpose of this paper to interpret phase equilibria data for three ternary solvent (1)–solvent (2)–polystyrene (3) systems in the light of present statistical–thermodynamic theory. Methyl ethyl ketone (1)–methanol (2)–polystyrene (3) (system I) was studied because of its frequent use in fractionation. The interaction parameters for each pair of components in this system are unknown. Consequently, although the data may be used to determine the plait point for the infinite molecular weight polymer species, very little further information is gained in this case. System II, carbon tetrachloride (1)–cyclohexane (2)–polystyrene (3), on the other hand, is a convenient choice for checking phase equilibria theory. Two of the three interaction parameters are known from vapor pressure and liquid–liquid equilibria measurements.[4] The "co-solvent"–polymer system, ethylcyclohexane (1)–cyclohexanol (2)–polystyrene (3) (system III), offered the peculiar advantage that all three pair interaction parameters were theoretically obtainable from liquid–liquid phase equilibria measurements.

Experimental

Materials.—The parent polymers were prepared by low conversion polymerizations of styrene monomer in bulk with thermal (for the highest molecular weight polymers) or benzoyl peroxide initiation. Polystyrene fractions were obtained by fractional precipitation of the polymer from dilute solutions in butanone by successive additions of methanol.[10] Table I lists the fractions, their intrinsic viscosities in benzene solution at 30°, molecular weights calculated by the relation[11]

$$\log M = 4.013 + 0.74 \log [\eta]$$

and their percentages of the parent polymers from which they were derived. The intrinsic viscosities were measured in Ubbelohde suspended-level viscometers. Kinetic energy corrections were applied throughout, but rate of shear corrections were unnecessary (rate of shear approximately 2000–2500 sec.$^{-1}$).

Reagent purity solvents were dried and distilled at least once through a 40-cm. glass helices-packed column.

Experimental Procedure.—Phase boundary curves were determined with the aid of a titration apparatus. This apparatus consisted of two Kimble Exax 5-ml. burets, graduated to 0.01 ml., with tips sealed into the head of a solution cell. The tops of the burets were fastened by rubber tube connectors, immersed in mercury wells, to vertical glass tubes, each having a three-way silicone-lubricated stopcock in the top bend. These vertical tubes were connected by approximately 0.8 meter lengths of rubber tubing to adjacent vertical tubes which could be raised and lowered. The lengths of rubber tubing and vertical glass tubes contained columns of mercury sufficient to prevent contact of vapor with the rubber on the buret side during all manipu-

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(1) This work constitutes a section of a thesis presented in partial fulfillment of the requirements for the degree of Doctor of Philosophy at Cornell University, by A. R. S.

(2) M. L. Huggins, *J. Chem. Phys.*, **9**, 440 (1941); *Ann. N. Y. Acad. Sci.*, **43**, 1 (1942); P. J. Flory, *J. Chem. Phys.*, **9**, 660 (1941); *ibid.*, **10**, 51 (1942).

(3) A. R. Shultz and P. J. Flory, THIS JOURNAL, **74**, 4760 (1952).

(4) A. R. Shultz and P. J. Flory, *ibid.*, **75**, 3888 (1953).

(5) L. H. Cragg and H. Hammerschlag, *Chem. Revs.*, **39**, 79 (1946).

(6) P. O. Powers, *Ind. Eng. Chem.*, **41**, 126, 2213 (1949); *ibid.*, **42**, 2558 (1950).

(7) R. L. Scott, *J. Chem. Phys.*, **17**, 268, 279 (1949).

(8) H. Tompa, *Trans. Faraday Soc.*, **45**, 1142 (1949); *ibid.*, **46**, 970 (1950).

(9) W. H. Stockmayer, *J. Chem. Phys.*, **17**, 588 (1949).

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

(11) R. H. Ewart, paper presented at the Atlantic City Meeting of the American Chemical Society, April 14, 1947.

lations of the vertically mobile tubes. The solution cell consisted of a titration head joined rigidly to the burets and a solution tube which was positioned in the equipment for each titration run. A rotary glass stirrer entered the cell through a mercury seal. Mercury in the well around the solution tube rim sealed the cell against vapor loss. The solution tube was immersed in a constant temperature water-bath regulated to ±0.01°.

The burets were filled by drawing the respective liquids into the apparatus through the buret tips. This was done by first raising the mobile tubes to their maximum heights, thus raising the contained mercury columns to their highest levels, then immersing the buret tips in the liquids, and lowering the tubes. The filled burets were allowed to stand at least 24 hours before use in order to saturate the atmosphere above the liquids with vapor and to reduce to a negligible rate vapor absorption by the small rubber surfaces. A polystyrene fraction was weighed into the solution tube, the tube was positioned under the titration head, and the mercury seals of the cell were filled. Initial readings of the burets were taken with the tips filled. Suitable amounts of the two liquids were admitted to the tube to effect solution of the polymer in a mixture near the precipitation point. Such a mixture was kinetically most favorable for dissolving the polystyrene because the relatively low viscosity of the resultant solution permitted adequate stirring. The transfer of liquids from the buret to the solution tube was accomplished by slowly raising the mobile tubes. The rising mercury columns transmitted pressure to the liquid surfaces in the burets through the intervening air and vapor columns. Very precise control was possible in this method of delivery.

The dissolving process usually required 45 to 90 minutes of stirring depending upon the molecular weight of the fraction and the polymer concentration desired. When solution was complete the precipitant was added dropwise until precipitation occurred. Precipitation was detected visually in the same manner as previously described.[3] Constant stirring was maintained throughout the precipitation runs. In system II the precipitation point was taken as the point of turbidity incidence upon addition of the precipitant, cyclohexane. However, in systems I and III the alcohols were too powerful as precipitants, so the precipitation concentrations were determined by adding methyl ethyl ketone, or ethylcyclohexane, to the point of clarity of a solution made turbid by one drop of alcohol. Higher dilutions of polymer were obtained by further additions of the two liquids. Thus precipitation measurements were performed at several polymer concentrations upon each polystyrene sample without opening the solution cell. The buret tips were fashioned to deliver approximately 0.01 ml. per drop. The volumes of solvent delivered from each buret were estimated to ±0.002 ml. The solution temperatures were controlled at 30.00, 15.00 and 56.80° (also 46.80°) for systems I, II and III, respectively. In all measurements the delivery temperatures of the burets were recorded and the proper corrections were made for density changes between delivery and solution temperatures. Concentrations were calculated ignoring possible volume changes upon mixing.

A preliminary determination of the approximate concentration region of total miscibility was made for system III. The precipitation temperatures of an unfractionated high molecular weight polystyrene ($\bar{M}_v \sim 3.0 \times 10^6$) were observed in several solutions of differing ethylcyclohexane–cyclohexanol ratios. The polymer concentration was not held constant, but varied over the range of polymer volume fractions ~0.02 to ~0.005.

Results.—The titration method of determining ternary phase boundary curves, as described above, yielded volume fractions accurate to approximately ±0.002. The accuracy was somewhat less for the higher polystyrene concentrations in which the volumes of the solvents used were small. Near and below $v_3 = 0.01$ some uncertainty in observing the point of phase separation was experienced due to the molecular weight heterogeneity existing within the fractions. The markedly different refractive indices of the phases separating in all three systems studied facilitated visual observations.

Theory and Discussion

The original thermodynamic treatment[2] of polymer solutions has been extended to ternary solvent (1)–solvent (2)–polymer (3) systems by Scott[7] and Tompa.[8] Their equations were derived for solvents possessing equal molar volumes. If this simplification is avoided the chemical potentials of the solvent species are given with greater generality by

$$\mu_1 - \mu_1{}^0 = RT[\ln v_1 + (1 - v_1) - (\mathrm{V}_1/\mathrm{V}_2)v_2 - (\mathrm{V}_1/\mathrm{V}_3)v_3 + (\chi_{12}v_2 + \chi_{13}v_3)(v_2 + v_3) - \chi_{23}(\mathrm{V}_1/\mathrm{V}_2)v_2v_3] \quad (1)$$

$$\mu_2 - \mu_2{}^0 = RT[\ln v_2 + (1 - v_2) - (\mathrm{V}_2/\mathrm{V}_1)v_1 - (\mathrm{V}_2/\mathrm{V}_3)v_3 + (\chi_{21}v_1 + \chi_{23}v_3)(v_1 + v_3) - \chi_{13}(\mathrm{V}_2/\mathrm{V}_1)v_1v_3] \quad (2)$$

where v_1, v_2 and v_3 are the volume fractions and V_1, V_2 and V_3 are the molar volumes of the respective components. The interaction parameters χ_{ij}[3,4,12] are per mole of the component represented by the first subscript.

We shall be concerned with the critical miscibility point for infinite molecular weight polymer in a ternary system. The solvent mixture corresponding to this point, which occurs at infinite polymer dilution (*i.e.*, at $v_3 = 0$), will be called the critical consolute mixture (CCM). From equations 1 and 2 Tompa has derived the following expression which relates the critical consolute mixture composition to the three pair interaction parameters[13]

$$l - 2lv_1{}^c\chi_{13} - 2l(1 - v_1{}^c)\chi_{23} + Dv_1{}^c(1 - v_1{}^c) = 0 \quad (3)$$

where $l \equiv (V_1/V_2)$, $v_1{}^c$ is the volume fraction of liquid 1 in the critical consolute mixture and

$$D \equiv 2\chi_{12}\chi_{13} + 2l\chi_{12}\chi_{23} + 2l\chi_{13}\chi_{23} - \chi_{12}{}^2 - \chi_{13}{}^2 - l^2\chi_{23}{}^2 \quad (4)$$

If the solvents have equal molar volumes (*i.e.*, if $l = 1$) equation 3 reduces to Scott's equation 30.[7]

System I: Methyl Ethyl Ketone (1)–Methanol (2)–Polystyrene (3).—The observed solution compositions at phase separation for three polystyrene fractions in system I at 30° are plotted in Fig. 1 using a triangular coördinate system, as is customary for three component systems. The data are presented on a small portion of the total triangular diagram in order to obtain a reasonable scale. The position of this enlarged rectangular portion in the total triangular diagram is shown by the shaded area of the inset. The curves for these finite molecular weight fractions do not intersect the methanol–methyl ethyl ketone base-line on the left as the data might appear to indicate. Instead, they should be expected to become essentially parallel to this base-line and to intersect the methanol–polystyrene edge of the triangular diagram at extremely low polymer concentrations. The lowest molecular weight fraction, PSN, shows the reversal of the phase boundary curve from steadily decreasing methanol volume fractions to increasing methanol concentrations below $v_3 = 0.01$.

No analytic method is known for extrapolating the observed phase boundary data for the various molecular weight polystyrene fractions to give the limiting binodial for infinite molecular weight. Empirical extrapolation can be performed satisfactorily, however, according to the graphical method shown in Fig. 2. Here the observed concentrations

[12] P. J. Flory and W. R. Krigbaum "Annual Reviews of Physical Chemistry," Vol. II, Annual Reviews, Inc., Stanford, California, 1951, p. 383 ff.

[13] H. Tompa, private communication. The left hand side of equation 3 has subsequently been obtained by the authors as a factor in an expression relating polymer coil extension to mixed-solvent composition.

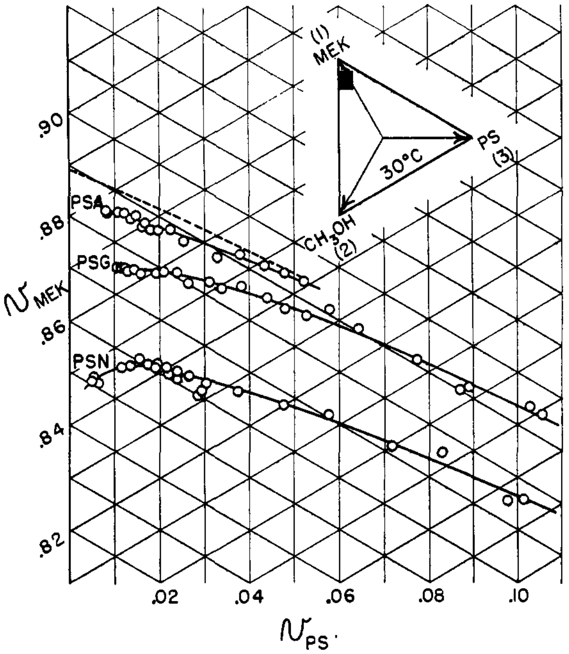

Fig. 1.—Phase boundary curves for system I at 30°. Volume fraction compositions at phase separation are given for mixtures of methyl ethyl ketone (1) and methanol (2) with three polystyrene fractions (3). The broken line represents the binodial for $M = \infty$.

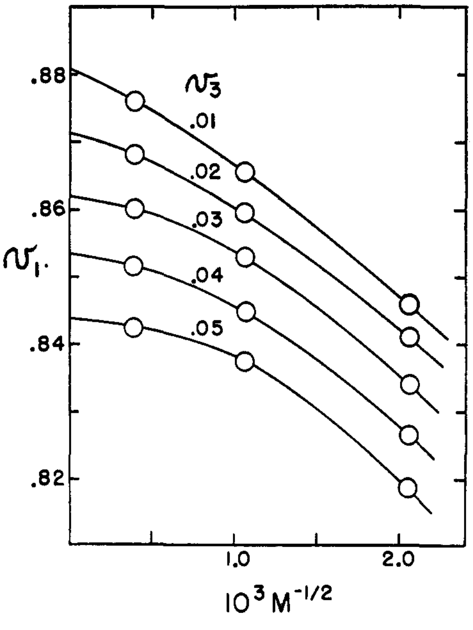

Fig. 2.—Methyl ethyl ketone volume fraction, v_1, at phase separation plotted against the reciprocal square root of the polymer molecular weight, $M^{-1/2}$, for five selected polystyrene concentrations, v_3. The intercepts define the respective methyl ethyl ketone concentrations on the $M = \infty$ binodial of system I.

of methyl ethyl ketone at precipitation of each of the polystyrene fractions at a given polymer concentration are plotted against the reciprocal square roots of the molecular weights $M^{-1/2}$ in analogy with the behavior of systems of two components.[3] The intercept at $M^{-1/2} = 0$ of each curve so formed gives the volume fraction of methyl ethyl ketone on the infinite molecular weight binodial at the chosen polystyrene concentration. The desired limiting binodial for $M = \infty$, obtained by plotting these intercept compositions, is represented by the broken line in Fig. 1. The extrapolation of this curve to zero polystyrene concentration yields $v_1^c = 0.889$, the volume fraction of methyl ethyl ketone in the critical consolute mixture.

Lacking satisfactory values for the pair interaction parameters in this system we attempt no evaluation of the theoretical significance of the critical consolute mixture observed. The intrinsic viscosities[14] of polystyrene fractions in this critical solvent mixture at 30° are proportional to the square roots of the polymer molecular weights in conformance with the predicted behavior in a solvent medium corresponding to the plait point for infinite molecular weight polymer.[15]

System II: Carbon Tetrachloride (1)–Cyclohexane (2)–Polystyrene (3).—The results of the precipitation titrations on this system are presented graphically in Fig. 3. The measurements were made at 15° where cyclohexane is a sufficiently strong precipitant. Since the region of partial miscibility at low polystyrene concentrations occurs near the cyclohexane apex of the triangular diagram, the form of the curves relative to the total diagram is easily discerned. The broken line in Fig. 3, representing the infinite molecular weight

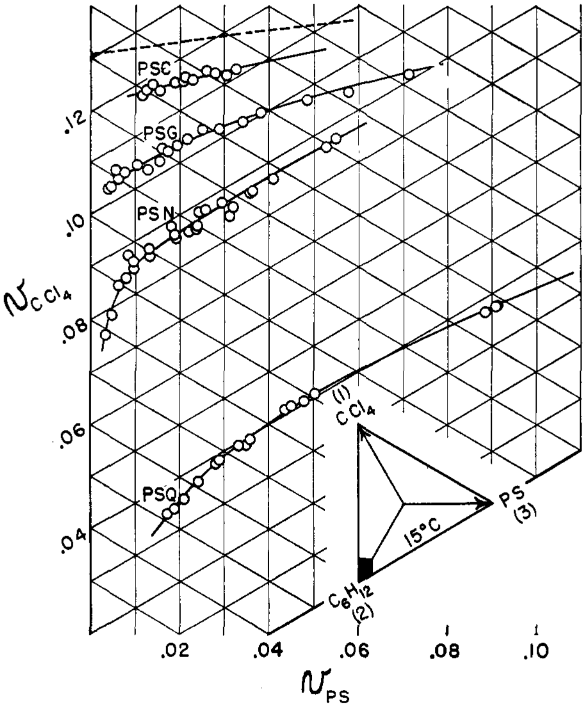

Fig. 3.—Phase boundary curves for system II at 15°. Volume fraction compositions at phase separation are given for carbon tetrachloride (1) and cyclohexane (2) mixtures with four polystyrene fractions (3). The broken line represents the binodial for $M = \infty$.

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(14) Data to be published.

(15) P. J. Flory, *J. Chem. Phys.*, **17**, 303 (1949); T. G. Fox, Jr., and P. J. Flory, *J. Phys. Colloid Chem.*, **53**, 197 (1949); P. J. Flory and T. G. Fox, Jr., This Journal, **73**, 1904, 1909 (1951).

polystyrene binodial, was obtained by the extrapolation procedure described above. The critical consolute mixture determined by extrapolation of this binodial to $v_3 = 0$ has carbon tetrachloride volume fraction $v_1 = 0.131$.

TABLE I

Fraction	$[\eta]$. 30° benzene	$M \times 10^{-3}$	Parent polymer, %
PSA	9.40	5500	3.3
PSC	7.75	4210	21.7
PSG	2.43	881	7.0
PSL	1.07	289	17
PSN	0.92	236	1.5
PSQ	0.428	84	17.5

Solution of equation 3 for χ_{13} and substitution of the values[4] $\chi_{12} = 0.109$, $\chi_{23} = 0.570$ and $l = 0.893$ yields $\chi_{13} = -0.125 \pm 0.05$ as the physically significant solution. This calculated carbon tetrachloride–polystyrene parameter corresponds closely to the carbon tetrachloride (i)–toluene (j) parameter[4] $\chi_{ij} = -0.14 \pm 0.04$ at 15°. Precise calorimetric measurements may in the future reveal a slightly exothermal mixing for the carbon tetrachloride–polystyrene pair as has been reported for carbon tetrachloride–toluene mixtures.[16] It should be noted that the negative interaction parameter indicates that carbon tetrachloride is a thermodynamically "good" solvent for polystyrene. Assuming[4] a small positive interaction parameter for the pair benzene–polystyrene one would predict a slightly higher intrinsic viscosity for a polystyrene fraction in carbon tetrachloride than in benzene at the same temperature. The failure of this prediction[14] remains unexplained at present.

System III: Ethylcyclohexane (1)–Cyclohexanol (2)–Polystyrene (3).—The precipitation temperatures of dilute solutions ($v_3 \sim 0.005$ to 0.02) of an unfractionated, bulk-polymerized polystyrene sample ($\bar{M}_v \sim 3.0 \times 10^6$) in ethylcyclohexane–cyclohexanol mixtures are plotted against the mixed solvent compositions in Fig. 4. The single-phase region lies above the curve. Below about 68° the polystyrene does not form a single-phase binary system of the same polymer concentration with either of the solvents alone. This enhanced solubility in mixtures as compared to the pure components is referred to as *cosolvency*. The curve in Fig. 4 indicated the possibility of obtaining two critical consolute mixtures for system III at 320°K. (46.8°). Binodials (not presented in this paper) for polysty-

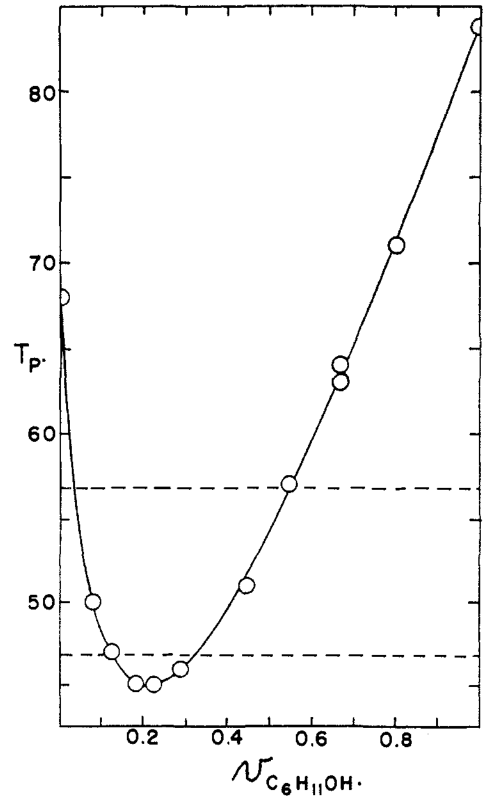
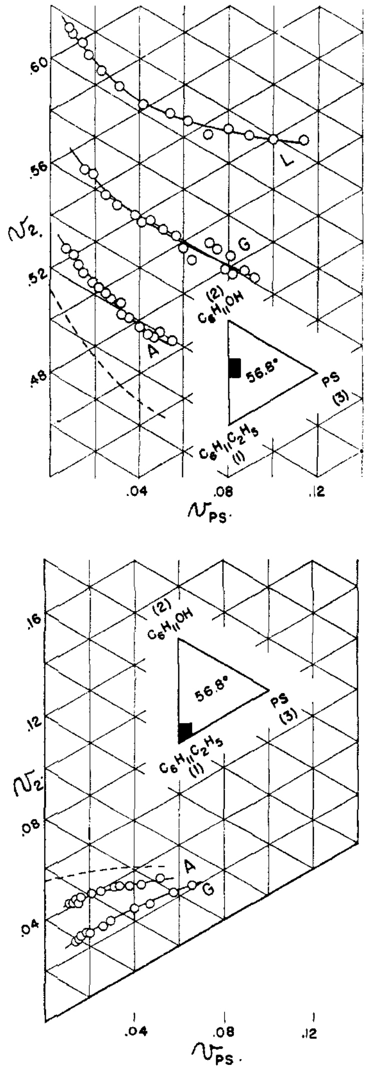


Fig. 4.—Precipitation temperatures, T_p, for dilute solutions of an unfractionated polystyrene sample ($\bar{M}_v \sim 3.0 \times 10^6$) plotted against the volume fraction of cyclohexanol in ethylcyclohexane–cyclohexanol mixtures.



Figs. 5a and 5b.—Phase boundary curves for system III at 56.8°. Volume fraction compositions at phase separation are given for ethylcyclohexane (1) and cyclohexanol (2) mixtures with three polystyrene fractions (3). The broken lines represent the binodials for $M = \infty$.

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[16] G. C. Schmidt, *Z. physik. Chem.*, **121**, 221 (1926).

rene fractions A, G and L in ethylcyclohexane–cyclohexanol mixtures were determined, therefore, at this temperature. Extrapolation of these data to obtain the infinite molecular weight binodials revealed that no critical consolute mixtures exist at 320°K. for this system. The curve of Fig. 4 lies somewhat below the curve for $M = \infty$ at zero concentration. Apparently this latter curve lies entirely above 320°K.

A desire to obtain a pair of critical consolute mixtures for this system prompted the determination of binodials for the same three polystyrene fractions at 330°K. Segments of the two regions of partial miscibility at this temperature are shown in Figs. 5a and 5b. Extrapolation of the data to $M = \infty$ was possible and the curves corresponding to those of Fig. 2 were essentially linear. The infinite molecular weight binodials thus obtained are represented by broken lines in Figs. 5a and 5b. Their extrapolation to infinite polymer dilution is complicated somewhat by their convexity to the ethylcyclohexane–cyclohexanol base-line. Admitting this possible source of error, we conclude that the two indicated critical consolute mixtures occur at v_1(CCM) = 0.488 and v_1(CCM) = 0.945 at 330°K.

Solving equation 3 for χ_{12} and substituting the values[4] $l = 1.357$, $\chi_{13} = 0.535$ and $\chi_{23} = 0.633$ yields $\chi_{12} = 0.44$ (or 2.35) for v_1(CCM) = 0.488. However, the same procedure yields conjugate complex solutions for χ_{12} at v_1(CCM) = 0.945. The value 0.44 is reasonable for the ethylcyclohexane–cyclohexanol interaction at 330°K. The reason for the failure of equation 3 to give a physically significant χ_{12} value at v_1(CCM) = 0.945 is to be found in the inadequacy of the chemical potential formulations used to describe mixtures containing an alcohol at low concentrations. Equations 1 and 2 do not even formally represent the desired chemical potentials in this concentration region. However, for the critical consolute mixture occurring at v_1(CCM) = 0.488 equations 1 and 2 should apply with sufficient accuracy to yield a satisfactory description of the plait point.

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Studies of the Diffusion of Mixed Solutes with the Gouy Diffusiometer

BY DAVID F. AKELEY AND LOUIS J. GOSTING

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In analyzing Gouy fringe patterns from two or more independently diffusing solutes it is convenient to separate certain time-dependent data, which provide a value of the height–area average diffusion coefficient, D_A, from the time-independent relative fringe positions, which contain all of the information about deviations of the boundary from Gaussian form. The latter data are conveniently recorded in the form of a graph of Ω_j, the relative fringe deviations from Gaussian positions, *versus* the reduced fringe numbers, $f(\zeta_j)$. Equations are developed which, when Ω_j is small, relate this graph to the fraction of the total gradient contributed by each solute and to ratios of the diffusion coefficients. A procedure for obtaining other average diffusion coefficients from D_A and this graph is also presented. Experiments with known mixtures of purified solutes confirm the validity of these methods of analysis. Since in favorable cases a few tenths of a per cent. of one solute as an impurity in another are detectable from the graph of Ω_j *versus* $f(\zeta_j)$, the Gouy diffusiometer can serve as a useful analytical tool. The application to protein diffusions of these methods for analyzing Gouy fringe patterns is illustrated by an experiment with bovine plasma albumin.

The purpose of this paper is to present new procedures for interpreting Gouy diffusiometer[1–6] data for mixed solutes and to test these procedures by experiments with known mixtures of purified compounds. It is expected that this work will be of particular utility in the study of proteins because most protein samples possess some heterogeneity,[7–13] and it is desirable that each protein diffusion experiment be analyzed to indicate the purity of the sample in addition to yielding an average diffusion coefficient. To illustrate the application of these methods to the study of proteins an experiment with crystallized bovine plasma albumin is included.

Equations which are derived for the analysis of mixtures also provide an estimate of the minimum amount of any impurity that can be detected with a given experimental error in the Gouy fringes. In support of these relations, experimental results show that a few tenths of a per cent. of potassium chloride in a sucrose sample produce measurable displacements of the Gouy fringes.

Theory

Three assumptions commonly made in studying the diffusion of mixed solutes in liquids[14–18] are used in the following development, the resulting

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[3] C. A. Coulson, J. T. Cox, A. G. Ogston and J. St. L. Philpot, *Proc. Roy. Soc.* (*London*), **A192**, 382 (1948).

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