

Swelling of Vulcanized Rubbers in Binary Solvent Mixtures

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Synopsis

The single-liquid approximation has been applied to the data of Bristow on the ternary systems containing benzene and cyclohexane with one of the rubbers, natural, SBR, or butyl. Satisfactory fits are obtained with a constant value of the interaction constant between the two solvents χ_{12} which differs markedly, however, from the value obtained by measurements on the binary solvent mixture.

Introduction

The swelling of vulcanized rubbers in mixtures of two solvents has been investigated by Krigbaum and Carpenter¹ and by Bristow.² In these investigations attention was focussed principally on the selective adsorption of one of the solvents by the polymer, the extension of the Flory-Huggins theory to mixtures of liquids by Krigbaum and Carpenter being apparently more readily tested by data of this type.

The more interesting feature, however, is the change in overall swelling with change in the composition of the solvent. The full theory¹ leads to a complex set of equations for determination of ϕ_3 , the volume fraction of the polymer in the swollen rubber phase. Bristow found that for many of the systems which he investigated the selective absorption of one solvent by the polymer was small, the composition of the solvent being almost the same in both phases, and it seems reasonable, therefore, to make use of the great simplification of the theory resulting from the assumption that the relative quantities of the two solvents in the liquid and swollen-polymer phases are equal. A similar treatment has been used by Scott³ to discuss phase relationships in a ternary system with one polymer component and was called by him the single-liquid approximation. For the case considered by Scott in which one of the low molecular weight liquids was a nonsolvent this approximation was rather unsatisfactory, but for the systems now being considered the lack of selective absorption of one solvent by the rubber means that the approximation must be much better.

For a binary system consisting of a single low molecular solvent 1 and a polymer 3 the Flory-Huggins theory involves a single interaction parameter χ_{13} , the value of which may be derived empirically. (The value is assumed to be independent of the polymer concentration but this is frequently only

true to a very limited accuracy.) The theory for the system solvent 1/solvent 2/polymer 3 involves not only the two solvent-polymer interaction constants χ_{13} and χ_{23} but also the solvent-solvent constant χ_{12} . The constants χ_{13} and χ_{23} will usually be obtained by swelling measurements using the pure solvents; χ_{12} may then be regarded as a disposable parameter which is to be used to fit the data for the swelling of the vulcanized polymer over a range of compositions of mixed solvents. The constant χ_{12} should be independent of the polymer and the theory will obviously be of limited use unless this is the case.

The only available data covering different polymers in the same pair of solvents are those of Bristow, who investigated the swelling of natural rubber, SBR, and butyl rubber in benzene-cyclohexane mixtures. In the present paper the theory of swelling with the single-liquid approximation is applied to these data.

Theory

A rather more general single-liquid approximation is required than is given by Scott³ for it is not to be assumed that the swelling liquids have equal molar volumes. The required equation, which is identical in form with that for a single liquid, is readily obtained from the treatment of Krigbaum and Carpenter¹ as

$$-RT [\ln (1 - \phi_3) + \phi_3 + \bar{\chi}\phi_3^2] = 2C\bar{V} [\phi_3^{1/3} - (\phi_3/2)]$$

where

$$2C = RT \nu / \phi_3 V_T'$$

C being the elastic constant as defined by Bristow and Watson,⁴

$$\bar{V} = (n_1 V_1 + n_2 V_2)$$

and

$$\bar{\chi} = \bar{V} \left(\frac{v_1 \chi_{13}}{V_1} + \frac{v_2 \chi_{23}}{V_2} - \frac{v_1 v_2 \chi_{12}}{V_1} \right)$$

$$\chi_{ij} = V_i A_{ij} / RT$$

The notation is that of Krigbaum and Carpenter, except that ν is taken as the number of moles of network chains in the swollen rubber; n_1 and n_2 are the mole fractions, and v_1 and v_2 the volume fractions of liquids 1 and 2 in the binary phase and V_1 and V_2 their molar volumes. ϕ_3 is the volume fraction of rubber in the swollen phase and V_T' the total volume of this phase. The A_{ij} are parameters giving the energy of ij -pair formation.

Application of the Theory to the Data of Bristow

Figure 1 shows the application of these equations to the data of Bristow. As Bristow does not give values of the elastic constant C for his vulcanizates, these were calculated from the swelling in the two pure solvents

using values of the interaction parameters χ_{12} and χ_{23} from Bristow and Watson. For natural rubber and butyl, χ_{12} was then chosen to give the best fit over the whole range of solvent composition (the values being 0.23 and 0.25). With the SBR the data for the two pure solvents gave discordant values for C . The curve shown was based on the assumption that the swelling in pure cyclohexane was correct and a value of 0.25 was used for χ_{12} . Bristow's data for the swelling of polychloroprene in the two pure solvents gave very widely discordant values of C , suggesting that one of the χ 's given is incorrect, and no attempt was made to fit the data for this polymer.

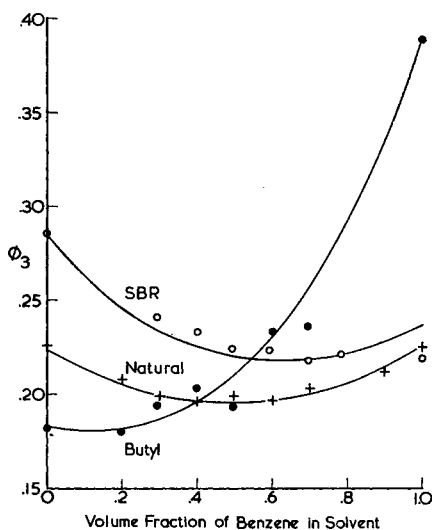


Fig. 1. Theoretical curves of swelling against solvent composition compared with experimental data of Bristow.

The data available for test of the theoretical relationship between swelling and solvent composition is very meagre but what exists can be fitted fairly satisfactorily with a single value of the interaction constant χ_{12} between benzene (1) and cyclohexane (2) of about 0.23–0.25. Bristow himself deduced a value of about 0.35 for the rubbers, natural, SBR, and polychloroprene, but 0.25 for butyl. Since the difference between solvent compositions in the two phases is small, the present method, although not particularly sensitive, would appear the more satisfactory for the determination of χ_{12} . The variation of swelling with solvent composition is probably of more practical interest than the composition of the solvent absorbed by the rubber.

The value of χ_{12} obtained in the present investigation accords even less well than Bristow's values with the value (0.47) obtained⁵ from vapor pressure measurements on benzene–cyclohexane mixtures. Nevertheless, the χ_{12} obtained from swelling measurements may be a useful empirical

parameter in the same way as χ_{13} and χ_{23} if it proves capable of correlating a variety of data.

References

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Résumé

L'approximation valable pour un liquide pur a été appliquée aux données de Bristow concernant les systèmes ternaires de benzène, de cyclohexane et d'un caoutchouc (naturel, SBR ou butyl). On a obtenu des résultats satisfaisants puisqu'on a trouvé une valeur fixe de la constante d'interaction entre les deux solvants χ_{12} . Elle diffère toutefois sensiblement de la valeur obtenue lorsqu'on effectue les mesures sur un mélange binaire de solvants.

Zusammenfassung

Die Einflüssigkeitsnäherung wurde auf die Ergebnisse von Bristow an ternären Systemen aus Benzol und Zyklohexan mit einem Natur-, SBR- oder Butylkautschuk angewendet. Genügende Übereinstimmung wurde mit einem konstanten Wert der Wechselwirkungskonstanten zwischen den zwei Lösungsmitteln χ_{12} erreicht, der sich aber deutlich von den durch Messungen der binären Lösungsmittelmischung erhaltenen Werten unterscheidet.

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