

The coalescence of polystyrene in correlated binary solvents

Quinn A. Besford[†], Maoyuan Liu[†], James K. Beattie[‡], Angus Gray-Weale^{†*}

[†] School of Chemistry, University of Melbourne, Victoria 3010, Australia

[‡] School of Chemistry, University of Sydney, NSW 2006, Australia

* Corresponding author: contact@gusgw.net

Dated: January 11, 2016

ABSTRACT:

The solution behaviour of solvophobic polymers is crucial to the development of polymer coatings and polymeric drug delivery vehicles. In this article, the role of dipolar interactions is investigated in the solvophobic coalescence of polystyrene in binary correlated polar solvent mixtures. A simple model for coalescence thermodynamics is derived from correlations between thermally rotating dipole moments in the solvent. The stabilising correlations lost to the solvent due to a solute's presence give rise to a driving force for the coalescence of solutes. This stabilisation is offset by the entropy of mixing that favours the dispersion of solutes. Predictions are compared to the measured point of coalescence of polystyrene in acetone when different alcohols are titrated. The model is shown to capture this point of coalescence and conformation for a variety of systems. Our results suggest the significant property determining the solubility of non-polar polymers in a polar liquid is a free energy resulting from attractive dispersion interactions between thermally rotating solvent dipole moments.

Keywords: solvophobe, solvophobic, coalescence, dipole, polystyrene, correlations

This is the author manuscript accepted for publication and has undergone full peer review but has not been through the copyediting, typesetting, pagination and proofreading process, which may lead to differences between this version and the [Version record](#). Please cite this article as [doi:10.1002/polb.24003](https://doi.org/10.1002/polb.24003).

INTRODUCTION

The solution behaviour of polymers is a strong function of both solvent type and solvent-polymer interactions. A working understanding of these interactions is needed to better understand phenomena such as membrane interactions, drug delivery, and plastics recycling. Interactions between solvents and solutes can be characterised by the Flory-Huggins χ^{FH} ^{1,2}, Hildebrand³, and/or Hansen⁴ solubility parameters. Parameters like these can provide a qualitative, if not quantitative, rationale with which to interpret solubility experiments. We seek a molecular mechanism connecting macroscopic miscibilities and solubility parameters with a free energy computable from molecular interactions within the solvent. This article will investigate free energies resulting from solvent dipole correlations, and show how these correlations can drive solvophobic solutes to coalesce.

The hydrogen bond is an attraction between a hydrogen atom from a molecule or molecular fragment, X-H, in which X is more electronegative than H, and an atom or group of atoms in the same or a different molecule, in which there is evidence of bond formation⁵. Hydrogen bonds were first understood through solubility studies^{6,7}, and the process of making and breaking hydrogen bonds in the condensed phase has been probed by a variety of experimental techniques and simulations^{8,9}. Hydrogen bonding alone, however, does not provide a consistent framework for the understanding of solubility in and the miscibility of liquids. For instance, acetone, a strong hydrogen bond acceptor¹⁰, has a very high dipole moment and is miscible with water and methanol (hydrogen bond donors¹⁰), but also miscible with heptane. In contrast, neither water or methanol is miscible with heptane at appreciable mole fractions^{11,12}. Ethyl acetate has a similar dipole moment to water and methanol, and is soluble in heptane and methanol, but not in water¹³. These inconsistencies suggest there is something more to solubility than dipole moments and hydrogen bonding.

Marcus¹⁴ tabulated a list of 120 solvents and classified them as structured or unstructured, by evaluation of two parameters: the entropy of vaporisation, $\Delta S_{vap}^o/R$, and the Kirkwood g -factor, g_K . If $\Delta S_{vap}^o/R \leq 11.6$ the solvent was considered unstructured based on Trouton's constant criterion, and if $g_K \leq 1.3$ it was considered unstructured on the basis of Kirkwood's dipole correlation criterion. The g_K parameter captures the intermolecular

many-body orientational correlation between dipole moments. Both these criteria have to be met for a solvent to be considered structured. A “structured solvent”, as described by Marcus, is a solvent that has strong dipole correlations. The “ordering” is related to the deficit in entropy the solvent has in comparison with a solvent of the same size and shape but devoid of structure¹⁵. Oster and Kirkwood¹⁶ suggested that the correlation parameter, g_K , is more significant than the molecular dipole moment as a basis for classification of liquids according to their thermodynamics. Oster and Kirkwood’s work showed that the orientational correlation is not determined by molecular dipoles alone, but also by the location of the permanent charge distribution in the interior of the polar molecule. This may aid in understanding the inconsistencies with acetone and ethyl acetate discussed above.

Gold and Perrine¹⁷ used the Kirkwood-Frohlich equation¹⁸⁻²⁰ and the resulting correlation parameter, g_K , to evaluate the level of dipole correlation in mixtures of carbon tetrachloride and alcohol. This provided an analysis of the dependence of dipole correlation with composition for the mixture of a “self-correlating” solvent (alcohol) with a non-correlating solvent (carbon tetrachloride). Gold and Perrine found the g_K to be a sensitive indicator of the steric effects due to size-shape changes found in the homologous alcohol group, in apparent agreement with Oster and Kirkwood’s conclusion on the location of the permanent charge distribution. Following Gold and Perrine’s work, we report an investigation of composition limits of binary mixtures of non-correlating and self-correlating solvents for which simple non-polar solutes become insoluble. The solvent mixtures studied consists of the non-correlating acetone, which initially solvates the nonpolar polystyrene, a common model “solvophobe”²¹, and first few small alcohols which are self-correlating ($g_K > 1$). We use this experimental system to test the validity of our dipole correlation model for solvents other than water (see Liu *et al.*²²).

We begin with a derivation for dipolar correlations in solvents, and a method for the calculation of lost interactions due to a solute’s presence. The strength of this effect is compared to the Flory-Huggins solubility parameter for polystyrene in a variety of solvents, and the model’s predictions then compared to experiments for the point of solvophobic coalescence of polystyrene in correlated binary solvent systems.

THEORY

Recently, we reported a dispersion contribution to the potential of mean force (PMF) between solvent molecules in a polar liquid due to the correlation between thermally rotating dipole moments²². The angular-dependent radial distribution function (RDF), g^{ij} , between two dipole moments, $\boldsymbol{\mu}_1$ of molecular species i and $\boldsymbol{\mu}_2$ of molecular species j separated by \mathbf{r} , may be given in terms of the angular dependent PMF as

$$g^{ij}(\mathbf{r}, \boldsymbol{\mu}_1, \boldsymbol{\mu}_2) = \exp(-\beta \mathcal{W}^{ij}(\mathbf{r}, \boldsymbol{\mu}_1, \boldsymbol{\mu}_2)), \quad (1)$$

where $\beta = (k_B T)^{-1}$, T is the absolute temperature, k_B Boltzmann's constant, and \mathcal{W}^{ij} is the PMF. The expansion of the angular-dependent functions in Equation 1 in the basis of rotational invariants²³, $\Phi_{l_1 l_2 l}(\mathbf{r}, \boldsymbol{\mu}_1, \boldsymbol{\mu}_2)$, gives

$$-\beta \mathcal{W}_S^{ij} - \sum_{l_1} \sum_{l_2} \sum_{l \geq |l_1 - l_2|}^{l_1 + l_2} \beta \mathcal{W}_{l_1 l_2 l}^{ij}(\mathbf{r}) \Phi_{l_1 l_2 l} = \log \left(g_S^{ij}(\mathbf{r}) + \sum_{l_1} \sum_{l_2} \sum_{l \geq |l_1 - l_2|}^{l_1 + l_2} h_{l_1 l_2 l}^{ij}(\mathbf{r}) \Phi_{l_1 l_2 l} \right), \quad (2)$$

where $h_{l_1 l_2 l}^{ij}$ is an expansion coefficient describing preferential modes of dipole orientations selected by $\Phi_{l_1 l_2 l}$, and the subscript "S" denotes the term independent of dipole orientation. The contribution of dipole correlations $h_{l_1 l_2 l}^{ij}$ to the angular averaged PMF, $\omega^{ij}(\mathbf{r}) = -k_B T \log(g_S^{ij}(\mathbf{r}))$, is expressed as

$$\omega^{ij}(\mathbf{r}) = \mathcal{W}_S^{ij}(\mathbf{r}) - k_B T \left\langle \log \left(1 + \sum_{l_1} \sum_{l_2} \sum_{l \geq |l_1 - l_2|}^{l_1 + l_2} \frac{h_{l_1 l_2 l}^{ij}(\mathbf{r})}{g_S^{ij}(\mathbf{r})} \Phi_{l_1 l_2 l} \right) \right\rangle_{\boldsymbol{\mu}_1, \boldsymbol{\mu}_2}. \quad (3)$$

The expansion of the logarithm in Equation 3 to the second order in rotational invariants for correlations between pairs of solvent molecules, i.e. $i = j = s$, yields

$$\omega^{ss}(\mathbf{r}) = \mathcal{W}_S^{ss}(\mathbf{r}) + \phi(\mathbf{r}) + O((h_{l_1 l_2 l}^{ss}(\mathbf{r}))^3 / (g_S^{ss}(\mathbf{r}))^3), \quad (4)$$

$$\phi(\mathbf{r}) = -k_B T \frac{1}{2(g_S^{ss}(\mathbf{r}))^2} \sum_{l_1} \sum_{l_2} \sum_{l \geq |l_1 - l_2|}^{l_1 + l_2} (h_{l_1 l_2 l}^{ss}(\mathbf{r}))^2, \quad (5)$$

where $\phi(\mathbf{r})$ is an orientation-independent contribution to the PMF arising from orientational correlation between dipoles. Since $\phi(\mathbf{r})$ is always negative, it produces an attractive force

between pairs of polar molecules. The slowest decaying pair correlation function in the $h_{l_1 l_2 l}$ set is the h_{112} function, given as²³

$$\lim_{r \rightarrow \infty} h_{112}(r) = \sqrt{\frac{2}{3}} \frac{(\epsilon - 1)^2}{4\pi y \rho \epsilon} \frac{1}{r^3}, \quad (6)$$

where $y = 4\pi\rho\mu^2/9k_B T$, ρ is the number density, and ϵ is the static permittivity. From Equation 6, we derived an exact asymptotic expression for $\phi(r)$ ²², given as

$$\phi_\infty(r) = \lim_{r \rightarrow \infty} \phi(r) = -\frac{k_B T}{2} \left(\lim_{r \rightarrow \infty} h_{112}(r) \right)^2, \quad (7)$$

$$= -k_B T \frac{27g_K^2(\epsilon - 1)^2}{16\pi^2(1 + 2\epsilon)^2\rho^2} \frac{1}{r^6}, \quad (8)$$

$$= -k_B T \frac{27g_K^2}{64\pi^2} \left[1 + O\left(\frac{1}{\epsilon}\right) \right] \frac{1}{\rho^2 r^6}, \quad (9)$$

where g_K is the Kirkwood g -factor. Equation 8 is an exact result for the potential of mean force between two thermally rotating dipole moments. In this article, it is this $\phi_\infty(r)$ interaction that is incorporated into a model for the coalescence of polystyrene in binary systems.

For use in binary solvent systems, Equation 8 must be expressed in terms of the properties of a mixed solvent system. This is done through the simplest generalisation of the method used by Marcus¹⁴ for g_K , by inclusion of a mixing rule for dipole moments and densities into the Kirkwood-Frohlich equation so as to obtain an ‘‘effective’’ g_K , g_e , as

$$g_e = \frac{(\epsilon - \epsilon_\infty)(2\epsilon + \epsilon_\infty)}{\epsilon(2 + \epsilon_\infty)^2} \left(\frac{4\pi}{9k_B T} (\mu_1^2 \rho_1 x_1 + \mu_2^2 \rho_2 (1 - x)) \right)^{-1}, \quad (10)$$

where $\epsilon_\infty = 1.1n_D^2$, and n_D is the refractive index. This allows for the calculation of g_e from pure state densities and dipole moments, and the dielectric constant²⁴ and the refractive index²⁵ of the mixture.

The effective contribution of dipole correlations to the PMF between two polar solvent molecules is then

$$\phi_e(r) = -k_B T \frac{27g_e^2(\epsilon - 1)^2}{16\pi^2(2\epsilon + 1)^2\rho^2} \frac{1}{r^6}. \quad (11)$$

The contribution of $\phi_e(r)$ to the solvation free energy of a solute is the amount of lost $\phi_e(r)$ interactions upon replacing a volume of solvent with a solute cavity. We approximate the

solute cavity as a sphere, and assume that the distribution of solvent molecules outside the cavity to be uniform. This first approximation is supported by simulation studies²², and does not change the dependence of free energy on size²⁶. The amount of lost correlation is then a two-body integral, expressed as

$$\frac{\Delta G_{\phi_e}(R)}{Nk_B T} = \frac{1}{2k_B T} \int d\mathbf{r} \int d\mathbf{r}' (\rho(R; \mathbf{r})\rho(R; \mathbf{r}') - \rho_0^2) \Theta(|\mathbf{r} - \mathbf{r}'| - d) \phi_e(|\mathbf{r} - \mathbf{r}'|), \quad (12)$$

where ρ_0 is the bulk density, Θ is the Heaviside step function where $\Theta(x) = 1$ for $x > 0$ and $\Theta(x) = 0$ for $x < 0$, $\rho(R; \mathbf{r}) = \rho_0 \Theta(|\mathbf{r}| - R)$ is the density distribution of solvent around a cavity of radius R , and $\Theta(|\mathbf{r} - \mathbf{r}'| - d)$ enforces a distance of closest approach of d between two solvent molecules measured from their centres. Note that d here is an effective distance of closest approach in the context of a binary solvent, where d satisfies the condition $4\pi\rho_0 d^3/3 = 1$. The form of d is derived from equating the integral of $\rho_0 \Theta(|\mathbf{r}| - d)$ over all space with the integral over all space of the $g(\mathbf{r})$ of an incompressible and homogenous liquid (see equation 2.5.32 of Hansen and McDonald second edition). This choice of d coincides with the definition of a ‘‘Gibbs dividing surface’’ between two particles in an incompressible fluid. Equation 12 was solved numerically with routines in Mathematica. The method of Equation 12 is derived and justified by Hansen and McDonald²³. The free energy of solvation therefore depends on the size of the cavity that the solute occupies, and can be shown to scale with the volume of the cavity at small R , and scale with the surface area of the cavity at large R (see supporting information of Liu *et al.*²²). Several small cavities may combine into a single large cavity to minimise the total ΔG_{ϕ_e} , therefore demonstrating a driving force for solute coalescence. The difference between coalescence or dispersion of solutes is found by

$$\frac{\Delta \Delta G_{\phi_e}(R_c, R_d)}{Nk_B T} = \left(\frac{R_d}{R_c} \right)^3 \Delta G_{\phi_e}(R_c) - \Delta G_{\phi_e}(R_d), \quad (13)$$

where R_d and R_c are the radii of the dispersed and coalesced particles, respectively. The size of dispersed particles R_d is defined similarly to the size of solvent particles d , given by $4\pi\rho_d R_d^3/3 = 1$, where ρ_d is the number density of the pure solute phase. Coalesced particles are assumed to be spherical here, given that two or more flexible polymers upon coalescence may rearrange and form a combined sphere. The size R_c therefore scales with $n^{1/3} R_d$, where

n is the number of solute particles that have coalesced.

The entropy of mixing, as in Flory-Huggins theory²⁷, is given by

$$\frac{S_{mix}}{k_B} = -M [x \ln(x) + (1-x) \ln(1-x)], \quad (14)$$

where M is the total number of spheres and x is the number fraction of one type of the spheres. Relating this to the aim here, x represents the mole fraction of polymer. This can also be expressed as a quantity per solvophobe molecule, which is a function of only x . Denoting this function s , it is found by

$$s(x) = \frac{S_{mix}}{k_B N} = -\ln(x) - \frac{1-x}{x} \ln(1-x), \quad (15)$$

where $N = Mx$ denotes the number of solute molecules. The configuration cost of coalescence per solvophobe is therefore

$$\frac{\Delta S_{mix}}{k_B N} = \frac{x_c}{x} s(x_c) - s(x), \quad (16)$$

where $x_c = (R_d/R_c)^3 x$. This change in entropy is negative for $R_c > R_d$. Combining Equation 16 and Equation 13, the total free energy change, with neglect of electrostatic and London dispersion forces, for the coalescence of solvophobe molecules is dependent on the solvent properties (g_e, ρ, ϵ), the size of the solvophobe (R_d), the mole fraction of solvophobe (x), and the size of the droplet (R_c),

$$\frac{\Delta G_c}{N k_B T} = \frac{\Delta \Delta G_{\phi_e}}{N k_B T} + \frac{\Delta S_{mix}}{N k_B}. \quad (17)$$

All parameters in the Equation 17 can be calculated from experimental properties of solvent or solute phases, with the exception of $R_c = n^{1/3} R_d$, where n is an independent variable. The variation of ΔG_c with n will reveal if a free energy barrier is present in the coalescence of particles, and the height of this barrier will control the likelihood of coalescence analogous to the classical nucleation theory.

EXPERIMENTS

Coalescence was determined by dynamic light scattering (DLS) with a Brookhaven Zeta Plus potential analyser with a detection angle of 90° and a 35mW laser. The polystyrene was confirmed as coalesced when the DLS count rate increased by orders of magnitude along with the stabilisation of the first order auto-correlation function, showing that particles of detectable size exist as opposed to a fluid of dissolved polymers. The polystyrene/acetone solutions were prepared in glass vials (sealed after addition of acetone) and stirred vigorously to dissolve. The alcohols were added *via* syringe in a titration manner. Once alcohol was added the solutions were again stirred vigorously at 298K. Polystyrene was obtained from Tosoh Bioscience in a variety of monodisperse molecular weight (M_W) standards. Acetone, methanol, and ethanol were spectroscopy grade solvents.

RESULTS and DISCUSSION

The hypothesis to be tested is that the interaction $\phi(r)$, given above as Equation 8, has a significant influence on, or controls, coalescence of polystyrene in solution. A stronger $\phi(r)$ interaction would favour coalescence by strengthening solvent-solvent attractions. We report two tests of this hypothesis. First, if $\phi(r)$ does affect solubility, then the measured solubility should correlate with the strength of $\phi(r) \propto g_e^2 \frac{(\epsilon-1)^2}{(2\epsilon+1)^2}$. We report the correlation of solubility parameters with this strength and with other interaction strengths. Second, we test the free energy change of coalescence due to $\phi(r)$, Equation 17, by measuring the composition limit at which coalescence occurs.

Flory-Huggins χ^{HF}

The solubility of solutes in various solvents has been quantified by parameters such as the Flory-Huggins χ^{FH} parameter, which was the first semi-quantitative interpretation of the behaviour of high polymer solutions^{1,2,13}. This theory is based on statistical mechanical analyses of a polymer solution using a lattice model, where it was shown that the free energy of mixing a polymer in a solvent is

$$\Delta G_m = RT [n_1 \ln(v_1) + n_2 \ln(v_2) + n_1 v_2 \chi_{12}^{FH}], \quad (18)$$

where n is the number of moles, v the volume fraction, R the ideal gas constant, and χ^{FH} the interaction constant between species 1 and 2 for the enthalpic change in free energy in interdispersing the polymer into the solvent. The physical meaning of three different regions of values for χ^{FH} is shown conceptually in Figure 1, where $\chi^{FH} < 0.5$ indicates the polymer spreads in the liquid (polymer-solvent interactions are greater than polymer-polymer and solvent-solvent interactions), $\chi^{FH} \approx 0.5$ indicates a θ solvent where the polymer adopts a random walk conformation, and $\chi^{FH} > 0.5$ indicates that the polymer-solvent interactions are not greater than the polymer-polymer and solvent-solvent interactions, and therefore the polymer collapses. This parameter is consequently a measure of the solvophobic effect. The χ^{FH} is an empirical parameter that describes solvophobic interactions, therefore if χ^{FH} correlates with an intermolecular force, that force is a strong contributor to solvophobic interactions.

Given that χ^{FH} can be used as a measure of the solvophobic effect, a simple analysis for the determination of the main cause of solvophobic coalescence is to compare χ^{FH} to the strength of the intermolecular forces present in the solvents. For the most general comparison, the relative strength of London dispersion forces (dispersion forces between two induced dipole moments²⁸), given by

$$F_{London} \propto \frac{(n_D^2 - 1)^2}{(n_D^2 + 1)^{(3/2)}}, \quad (19)$$

of Lifshitz dipolar dispersion forces (dispersion forces between two permanent dipole moments, and between a permanent dipole moment and an induced dipole moment²⁸), both given by

$$F_{dipolar} \propto \frac{(\epsilon - 1)^2}{(\epsilon + 1)^2}, \quad (20)$$

along with that stemming from $\phi(r)$ (Equation 8), are compared to the χ^{FH} for polymer polystyrene in a variety of polar and non-polar solvents in Figure 2, along with the g_K by itself. The London dispersion strength is calculated from the refractive indices n_D of the

liquids, whereas the Lifshitz dipolar dispersion forces are based on the static permittivity ϵ , and the $\phi(r)$ interaction is based on both the static permittivity and the Kirkwood g -factor g_K .

The experimental data comes from a variety of sources, determined *via* different methods; Etrede²⁹ reports χ^{FH} for polystyrene determined by a gravimetric method; Gunduz and Dincer³⁰ reports χ^{FH} values determined by gas chromatography; and Orwoll and Arnold³¹ tabulated χ^{FH} values determined by osmotic pressure, vapour sorption, and inverse gas chromatography measurements. The χ^{FH} values are compared to the dimensionless strength of London dispersion interactions (Figure 2 A), dimensionless Lifshitz dipolar dispersion interactions (Figure 2 B), the Kirkwood g -factor, g_K (Figure 2 C), and to the dimensionless $\phi(r)$ interaction (Figure 2 D).

The comparison of χ^{FH} for polystyrene in Figure 2 gives a picture into which intermolecular force may be responsible for the solution behaviour of the solvophobic polystyrene in solution. There is no detectable correlation in comparing London dispersion and Lifshitz dipolar dispersion forces for the thermodynamics of interdispersing polystyrene in each of the solvents. This suggests that these interactions are not responsible, at least alone, for solvophobic behaviour. There is, however, a correlation between χ^{FH} and the g_K for each solvent. The strongest correlation is between χ^{FH} and the strength of $\phi(r)$. This demonstrates a link between the $\phi(r)$ interaction between solvent molecules and the solvophobic effect.

Polymer coalescence

The addition of a correlating solvent ($g_K > 1$) to a non-correlating solvent, for example adding an alcohol to acetone, gradually changes the degree of correlation to that of the pure correlating solvent. This does not occur linearly, Figure 3 shows a slower than linear increase in the overall effective dipole correlation, g_e , of the mixture. Further, the larger the alcohol the greater the mole fraction required to increase the overall g_e . This confirms the result reported by Gold and Perrine¹⁷ (see introduction). Any free energy resulting from g_e will also be non-linear with solvent composition.

The change in free energy for the aggregation of polystyrene in solution is estimated as

a function of solution composition (for ethanol), and of the number of polymers already aggregated, as shown in Figure 4, using Equation 17. The results in Figure 4 are for a constant mole fraction x of polystyrene of 10^{-5} , approximated as a Flory-Huggins polymer of 57 monomers. Figure 4 shows how the barrier height to a favourable change in free energy for coalescence, changes as the fraction of correlating solvent (ethanol) is increased. For the case of no ethanol present, the dispersion of polystyrene is always favoured with a positive change in free energy for coalescence. On the other hand, at 75% ethanol there is almost no barrier of coalescence to be overcome. Only a relatively small fraction of ethanol is required to strengthen the $\phi(r)$ interaction between solvents so that the free energy favours aggregation. Figure 4 shows that $\phi(r)$ along with the entropy of mixing together result in a solvophobic effect.

The goal now is to determine the mole fraction x of polystyrene that is required to reach the cloud point (point of coalescence) for polystyrene in an alcohol/acetone mixture. We must choose the height of the barrier that is sufficient to prevent coalescence, allowing the calculation for the mole fraction x of polystyrene required to reach coalescence as a function of both the M_W of the polymer and of the volume percentage of alcohol. This is calculated for the methanol/acetone system for polystyrenes of three different molecular weights and the results shown in Figure 5.

Experimentally there are data for polystyrenes of three different molecular weights at various mole fractions x , spanning a large region of the coalescence curves. Equation 17 allows prediction for these experimental data based on some minor assumptions; the size of the polystyrene is approximated as a Flory-Huggins polymer occupying 25, 57, and 98 sites on the lattice for the M_W of 2.6×10^3 , 5.9×10^3 , and 1.0×10^4 , respectively, and that the barrier height to coalescence is between 0.1 - 1 $k_B T$ (shown as the upper and lower bounds of the curves, respectively).

Figure 5 shows agreement between the model (Equation 17) and experimental data for the coalescence of polystyrene in binary solvents. The coloured bands indicate the range of the prediction by varying the barrier height to coalescence, where the top of the band indicates 0.1 $k_B T$, the bottom 1 $k_B T$, and the middle white band 0.4 $k_B T$. This choice of 0.4 $k_B T$ matches the experimental data the best. Other forces that are neglected may

alter the height of this barrier to coalescence, such as electrostatic repulsion between the polystyrenes. There is one outlier in the dataset for the $M_W = 2.6 \times 10^3$ polymer, which is not captured by theory. This simple experiment provides a method for the quantification of the solvophobicity of a solute in a liquid system.

As an alternative approach, given a known mole fraction x of polystyrene, then the volume fraction of alcohol required to coalesce the polystyrene particles in solution can be computed as a function of polystyrene M_W . This is shown in Figure 6 for the case of methanol and ethanol as titrants, compared to the cloud point of different molecular weight polystyrenes at a constant mole fraction ($x \approx 10^{-4}$). Like in Figure 5, in Figure 6 a range for the $\phi_e(r)$ interaction and Flory-Huggins entropy prediction is shown, where the lower band is $1 k_B T$ and the upper $0.1 k_B T$ for the barrier height to coalescence, where the middle white band in both plots is for $0.4 k_B T$. Both alcohols have different theoretical curves, primarily stemming from differences in g_e , where ethanol has a slightly lower g_e as a mixture with acetone and subsequently a larger volume fraction is required to cause polystyrene to become solvophobic and coalesce.

Agreement for both alcohols is found between theory and experiment. A number of experiments are done at the same mole fraction x to show the range of deviations. For the case of ethanol as the titrant, the $M_W = 6.0 \times 10^3 \text{ g mol}^{-1}$ is not captured by theory, hinting that the theoretical curvature for limiting/critical volume fraction vs. M_W may differ from the true curvature. However the curvature for the methanol system aligns well between theory and experiment. Considering the neglect of all other forces, besides $\phi(r)$ interactions and the entropy of mixing, we conclude $\phi(r)$ is a strong influence on the solubility of non-polar solutes.

These simple comparisons have shown that the main determining factor in driving solvophobic polymers together is the strength of $\phi(r)$ between solvent dipole moments. Adding alcohol to the acetone system strengthens the $\phi(r)$ interaction between dipole moments, due to the level of local correlation between alcohol dipole moments, captured through g_K , and it is this interaction that drives the coalescence of solvophobic solutes. The model may be improved by incorporating extra interactions such as London dispersion and electrostatic forces. The system studied was designed for there to be minimal changes in London disper-

sion forces, as all species present have approximately the same Hamaker interaction constants (see chapter 13 of the book by Israelachvili²⁸), and minimal electrostatic interactions as there are no ionic species present. The driving force for coalescence of polystyrene in these experiments is therefore distinct from London dispersion and electrostatic interactions. Since the predictions for coalescence of simpler solutes by $\phi(r)$ matches the given experiments, it is this $\phi(r)$ dipolar interaction that is the hitherto now missing driving force for solvophobic coalescence.

CONCLUSIONS

This solubility study of polystyrene has demonstrated that the solvophobic coalescence of simple solutes is largely determined by dipole correlations between solvent dipole moments. The model employed does not account for solvent-solute or solute-solute dipolar correlations, which for the case of a polar solute is likely needed. However, for the studied system of acetone, alcohol, and polystyrene, our model consisting of $\phi(r)$ interactions between solvent dipole moments and a mixing entropy, has well captured the experimental critical points between soluble and insoluble states for polystyrene.

ACKNOWLEDGMENTS

This research was supported by a grant from the Australian Research Council (Grant No. DP110103388). The Australian Government is acknowledged for Australian Postgraduate Awards (QAB and ML). QAB gratefully acknowledges the University of Melbourne for receipt of the Albert Shimmins Award.

References

1. P. J. Flory. *J. Chem. Phys.* **1941**. *9*(8), 660.
2. M. L. Huggins. *J. Chem. Phys.* **1941**. *9*(5), 440.
3. J. H. Hildebrand. *PNAS* **1979**. *76*(12), 6040–1.
4. C. M. Hansen. *Hansen Solubility Parameters: A User's Handbook*. Taylor & Francis Group, New York, 2nd edition, **2007**.
5. E. Arunan, G. R. Desiraju, R. A. Klein, J. Sadlej, S. Scheiner, I. Alkorta, D. C. Clary, R. H. Crabtree, J. J. Dannenberg, P. Hobza, H. G. Kjaergaard, A. C. Legon, B. Men-
nucci, D. J. Nesbitt. *Pure Appl. Chem.* **2011**. *83*(8), 1637–1641.
6. W. Nernst. *Z. Phys Chem* **1891**. *8*, 110–139.
7. G. Pimentel, A. McClellan. *The Hydrogen Bond*. W.H. Freeman and Company, San Francisco and London, **1960**.
8. A. Luzar, D. Chandler. *Letters to Nature* **1996**. *379*, 55–57.
9. J. Dore, J. Teixeira. *Hydrogen-Bonded Liquids*. Kluwer Academic, Dordrecht, **1991**.
10. M. Roscs, C. Rafols, J. Ortega, E. Bosch. *J Chem Soc Perking Trans* **1995**. *1*(2).
11. J. Polak, B. C.-Y. Lu. *Can. J. Chem.* **1973**. *51*(24), 4018–4023.
12. C. Savini, D. Winterhalter, H. Van Ness. *J. Chem. Eng. Data* **1965**. *10*(2), 171–172.
13. J. H. Hildebrand, R. L. Scott. *The Solubility of Nonelectrolytes*. Dover Publications, New York, 3rd edition, **1951**.
14. Y. Marcus. *J. Solution Chem.* **1992**. *21*(12), 1217–1230.
15. Y. Marcus. *J. Solution Chem.* **1996**. *25*(5), 455–469.
16. G. Oster, J. G. Kirkwood. *J. Chem. Phys.* **1943**. *11*(4), 175.

17. P. Gold, R. Perrine. *J. Phys. Chem.* **1967**. 71(13), 4218–4222.
18. J. G. Kirkwood. *J. Chem. Phys.* **1939**. 7(10), 911–919.
19. F. H. *Trans. Faraday Soc.* **1947**. 44(238), 238–243.
20. H. Frohlich. *Theory of Dielectrics*. Clarendon Press, Oxford, **1950**.
21. A. Faghihnejad, H. Zeng. *Soft Matter* **2012**. 8(9), 2746.
22. M. Liu, Q. A. Besford, T. Mulvaney, A. Gray-Weale. *J. Chem. Phys.* **2015**. 142, 114117–1–15.
23. J.-P. Hansen, I. R. McDonald. *Theory of Simple Liquids*. Academic Press, London, 2nd edition, **1986**.
24. A. V. Celiano, P. S. Gentile, M. Cefola. *J. Chem. Eng. Data* **1962**. 7(3).
25. M. Iglesias, B. Orge, M. Domínguez, J. Tojo. *Phys. Chem. Liq.* **1998**. 37, 9–29.
26. D. Chandler. *Nature* **2005**. 437(7059), 640–7.
27. P.-G. de Gennes. *Scaling concepts in polymer physics*. Cornell Univeristy Press, New York, **1979**.
28. J. N. Israelachvili. *Intermolecular and Surface Forces*. Academic Press inc. Elsevier, London, 3rd edition, **2011**.
29. L. a. Errede. *J. Appl. Polym. Sci.* **1992**. 45(4), 619–631.
30. S. Gunduz, S. Dincer. *Polymer* **1980**. 21, 1041–1046.
31. R. A. Orwoll, P. A. Arnold. In *Physical Properties of Polymer Handbook*, volume 50, chapter 14. Springer, New York, **2007**. 233–257.

Figure 1: A schematic demonstrating the meaning of the Flory-Huggins χ^{FH} solubility parameter.

Figure 2: A comparison of the Flory-Huggins solubility parameter χ^{FH} for polystyrene in a variety of solvents to the dimensionless strength of London dispersion and Lifshitz dipolar dispersion forces (top left and right, respectively), the Kirkwood g -factor (g_K) and $\phi(r)$ interaction (bottom left and right, respectively). The values of χ^{FH} come from three sources; solid diamonds from Gunduz and Dincer³⁰, hollow diamonds from Orwoll and Arnold³¹, and pointed hollow squares from Errede²⁹. Fits to the three separate sources of data and correlation coefficients are shown in their respective plots.

Figure 3: The overall change in the effective total dipole correlation, g_e , with changing composition from pure acetone to pure alcohol, as calculated from Equation 10.

Figure 4: The free energy barrier for the aggregation of a polymer as a function of solvent composition and of the number of polymers already aggregated. Data is calculated for a constant mole fraction x of polystyrene (10^{-5}) and only data for ethanol mixing with acetone is shown.

Figure 5: The amount of methanol (volume percentage) required to cause mole fraction x of polystyrene to coalesce in solution, for different molecular weight (M_W) polystyrenes. The experimental data is shown as hollow circles, colour depending on M_W , and theory is shown as colourful bands, as evaluated from Equation 17. The theory involves a choice of barrier height to coalescence, which a range of choices is shown from $0.1 k_B T$ to $1 k_B T$, with $0.4 k_B T$ showing best agreement with experiment (white lines). This system has a constant mole fraction x of polystyrene of 10^{-5} .

Figure 6: The volume fraction of alcohol (methanol top, ethanol bottom) required to coalesce polystyrene of a defined molecular weight M_W .

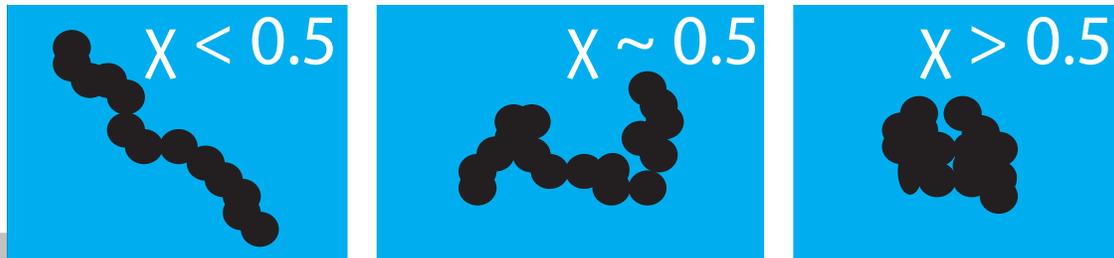


Figure 1
Quinn A. Besford[†], Maoyuan
Liu[†], James K. Beattie[‡], Angus
Gray-Weale^{†*}
J. Polym. Sci. B

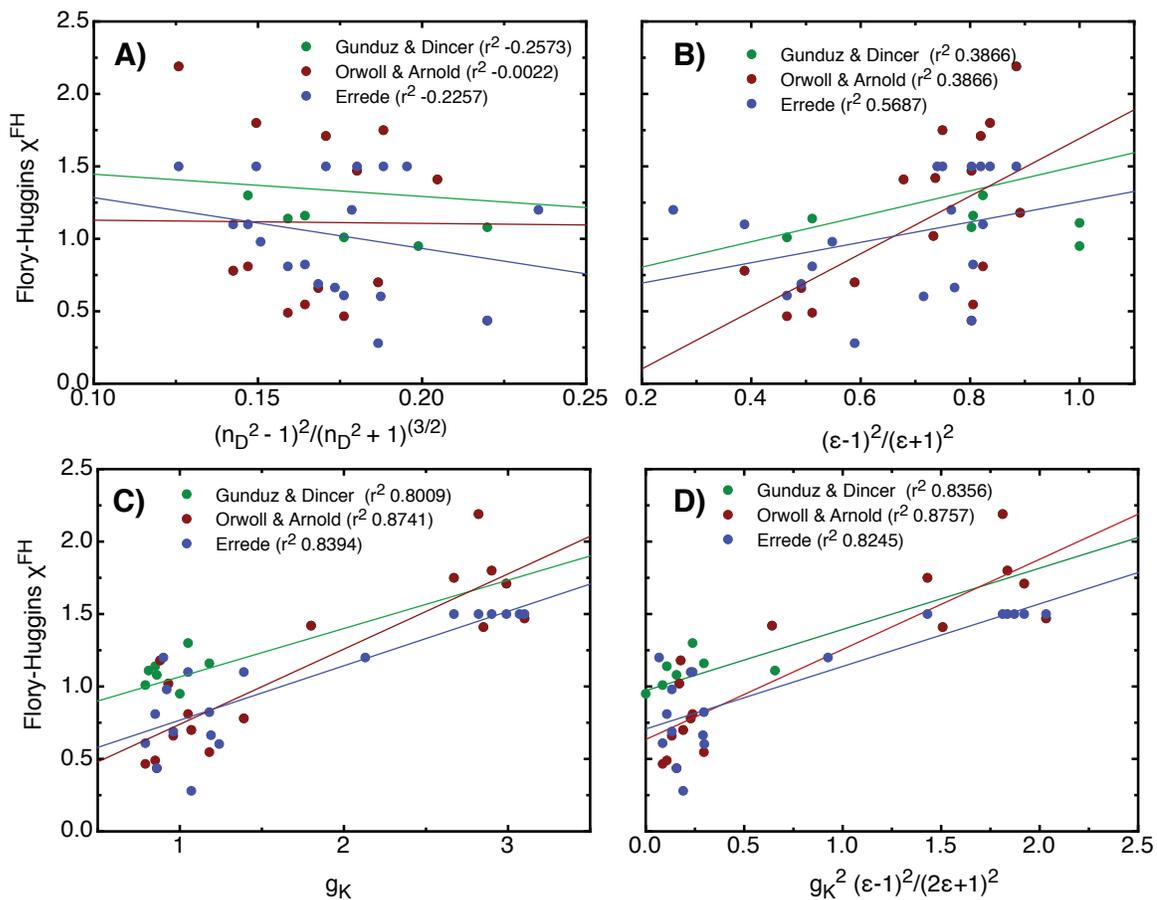


Figure 2

Quinn A. Besford[†], Maoyuan Liu[†], James K. Beattie[‡], Angus Gray-Weale^{†*}
J. Polym. Sci. B

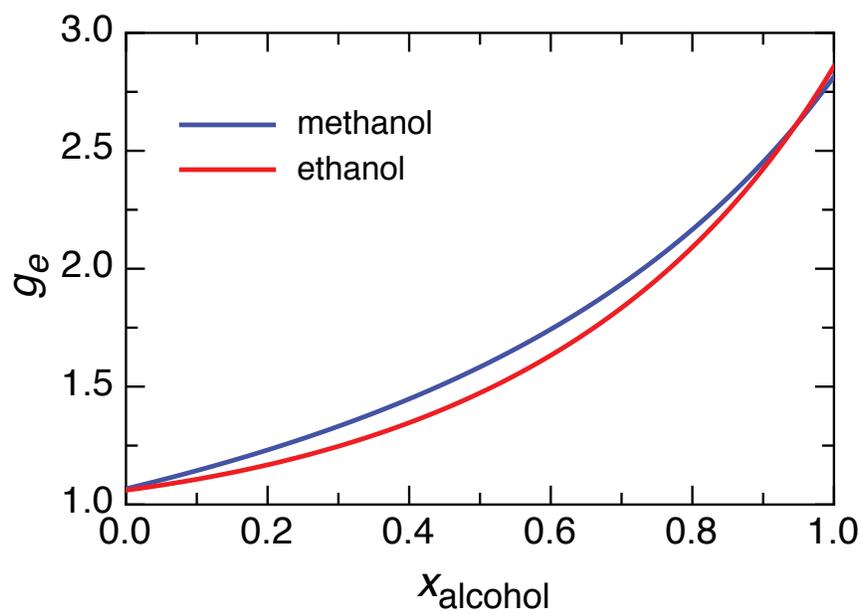


Figure 3
Quinn A. Besford[†], Maoyuan
Liu[†], James K. Beattie[‡], Angus
Gray-Weale^{†*}
J. Polym. Sci. B

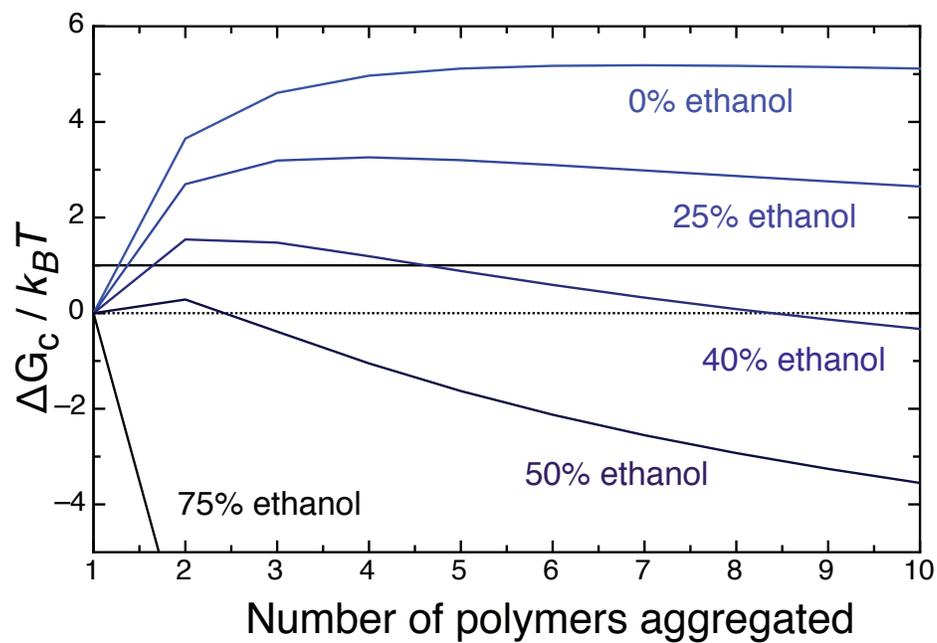


Figure 4
Quinn A. Besford[†], Maoyuan
Liu[†], James K. Beattie[‡], Angus
Gray-Weale^{†*}
J. Polym. Sci. B

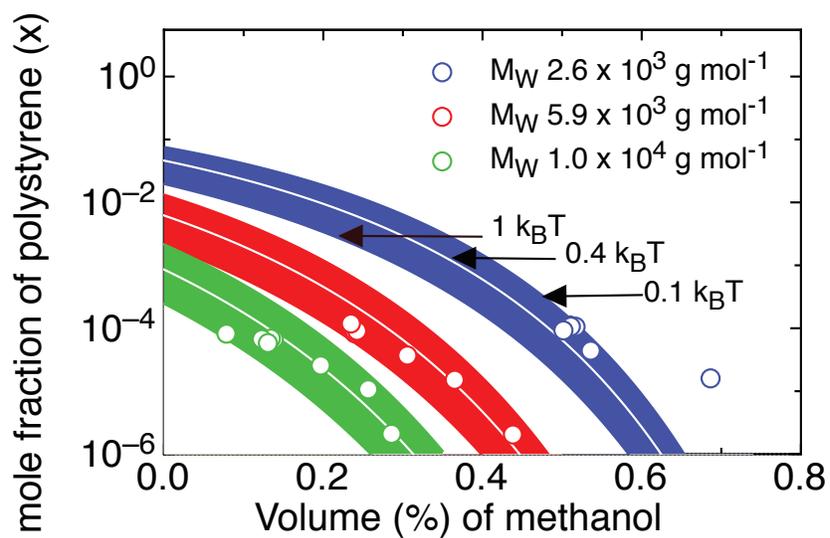


Figure 5
Quinn A. Besford[†], Maoyuan
Liu[†], James K. Beattie[‡], Angus
Gray-Weale^{†*}
J. Polym. Sci. B

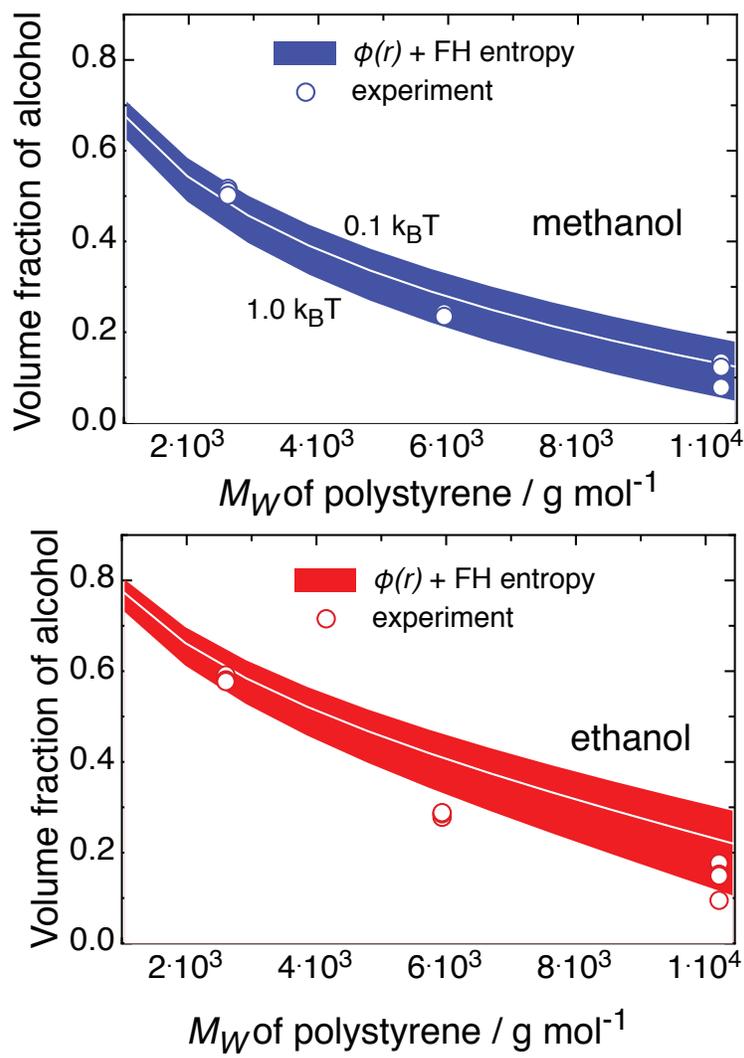


Figure 6
Quinn A. Besford[†], Maoyuan
Liu[†], James K. Beattie[‡], Angus
Gray-Weale^{†*}
J. Polym. Sci. B



Minerva Access is the Institutional Repository of The University of Melbourne

Author/s:

Besford, QA;Liu, M;Beattie, JK;Gray-Weale, A

Title:

The Coalescence of Polystyrene in Correlated Binary Solvents

Date:

2016-05-15

Citation:

Besford, Q. A., Liu, M., Beattie, J. K. & Gray-Weale, A. (2016). The Coalescence of Polystyrene in Correlated Binary Solvents. JOURNAL OF POLYMER SCIENCE PART B-POLYMER PHYSICS, 54 (10), pp.948-955. <https://doi.org/10.1002/polb.24003>.

Persistent Link:

<http://hdl.handle.net/11343/290932>