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Toward a Universal Approach To Enable Transfer of Equilibrium Constants in Hydrogen-Bonded Blends

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Over the past decade clear evidence has emerged that molecular architecture can alter functional group accessibility (FGA), which in turn affects phase behavior of hydrogen-bonded blends.[1–5] Thus, any model that attempts to predict phase behavior must take into account the effect of FGA. However, to date there are no models that can *a priori* predict FGA effects.

The phase behavior of hydrogen-bonded blends is often described using the modified form of the Flory−Huggins equation proposed by Painter and Coleman.[6] Briefly, the hydrogen-bonding contribution is written as a balance between self-association (B−B) (represented by equilibrium constant K_B) and interassociation (B−A) (represented by equilibrium constant K_A). A fundamental assumption of this model is that for copolymers K_A is constant irrespective of the composition, as long as the comonomer is "inert" (e.g., styrene, butadiene, etc.).[5] This implies that the value of K_A obtained for PVPh/PVAc (PVPh = poly(vinylphenol); PVAc = poly(vinyl acetate)) blends is valid for other PVAc copolymer blends (e.g., PVPh/EVAc (ethylene-*co*-vinyl acetate)). However, changes in the molar volume of the reference unit (B) must be taken into account. Thus, for DMVPh/EVAc (DMBVPh = dimethylbutadiene-*co*-vinylphenol) blends

$$\frac{K_{A_{\mathrm{DMBVPh/EVAc}}}}{K_{A_{\mathrm{PVPh/PVAc}}}} = \frac{V_{\mathrm{PVPh}}}{V_{\mathrm{DMBVPh}}} \tag{1}$$

where V_{PVPh} and V_{DMBVPh} are the molar volumes of PVPh and DMBVPh, respectively, while $K_{A_{\mathrm{PVPh/PVAc}}}$ and $K_{A_{\mathrm{DMBVPh/EVAc}}}$ are the interassociation equilibrium constants for PVPh/PVAc and DMBVPh/EVAc blends, respectively. Equation 1 signifies that introduction of inert groups such as dimethylbutadiene in the reference unit B alters hydrogen bonding simply due to dilution effects. However, recent experimental evidence clearly shows that factors such as accessibility of functional groups (FGA) can dramatically alter K_A.[2–5,9] For example, in blends of DMBVPh(24)/EVAc(x),[3] increase in backbone spacing between functional groups in polymer A ($x \downarrow$) increases K_A^{std}, suggesting improved FGA.[7] Additionally, for DMBVPh(24)/PAMA (poly(alkyl methacrylate)) blends, Pehlert et al.[2] demonstrated that as the length of the side chain in PAMA increased, K_A^{std} decreased, indicating decreased carbonyl group accessibility. Finally, Pehlert et al.[3,5] investigated the competing effects of "inert" spacing between carbonyl groups in the backbone versus the long side chains for the DMBAMA copolymers (DMBAMA = dimethylbutadiene-*co*-alkyl methacrylate).[4] Hence, in eq 1, besides dilution, one has to consider FGA to obtain the "real" value of K_A^{std}. From a predictability perspective, Pehlert et al.[3,5] proposed an empirical correlation that expressed K_A^{std} as a function of spacing between functional groups for DMBVPH/EVAc copolymer blends. Unfortunately, not much has been said about the use of this equation for other systems. To the best of our knowledge, we know of no model/approach which *a priori* can predict FGA effects on K_A^{std}. To summarize, FGA issues arise primarily due to the inability of the functional groups to rotate and form hydrogen bonds. Introducing chain extenders (inert groups such as ethylene units) between backbone functional groups increases chain flexibility and hence the ability to form hydrogen bonds. This is an inherently different effect from intramolecular screening considered previously,[8,9] which is primarily a result of polymer chain back-bending. In this communication we restrict ourselves to the effect of chain architecture on FGA.

It is our aim to develop a universal correlation (albeit empirical) that would permit easy transferability of equilibrium constants and in turn broaden the predictive nature of the association model. To do this, we need to understand the relationship of the effect of molecular architecture (FGA) on the resulting inefficiencies in chain packing which ultimately reduce intermolecular contacts. Recently,[10] we have been interested in packing effects on blend miscibility. In this regard we proposed a model to predict the effect of structural variations between blend repeat units (e.g., stereoisomerism) on polymer phase behavior without invoking equation of state arguments. The model successfully predicted the presence of both UCST and LCST in stereoregular poly(methyl methacrylate) (PMMA) blends.[9] In this communication using previously described concepts, we are able to provide for the first time a universal approach for predicting/transferring K_A^{std} in hydrogen-bonded blends.

We begin with Staverman's ideas, who suggested that intermolecular interactions are a function of accessible surface area instead of molar volume, which in turn is related to the number of contact points.[11] Flory, on the other hand, linked the number of possible intermolecular contacts in a mixture to surface to volume ratios (s) of the corresponding molecules.[12] Thus, we relate intermolecular interactions to s (surface/volume ratio). In polymer mixtures, in addition to "s", packing inefficiencies result due to chain connectivity. Also intuitively, we believe that the aspect ratio (Γ) of the Kuhn segment, i.e., ratio of the Kuhn length (b) to the diameter (d) ($\Gamma = b/d$), influences the accessible surface area (by affecting packing) and hence intermolecular interactions.

Using the arguments presented above, we propose the standard interassociation equilibrium constant, K_A^{std}, which is a function of FGA, is directly proportional to the product of the surface to volume ratio per repeat unit and the aspect ratio of the Kuhn segment length

$$\mathrm{FGA} \propto K_A^{\mathrm{std}} \propto s\Gamma \tag{2}$$

or

$$\frac{K_{A_1}^{\mathrm{std}}}{K_{A_2}^{\mathrm{std}}} = \frac{s_{A_1}\Gamma_{A_1}}{s_{A_2}\Gamma_{A_2}} \tag{3}$$

Here s_{A_1} and s_{A_2} are the surface to volume ratios and Γ_{A_1} and Γ_{A_2} are the aspect ratios of components A_1 and A_2, respectively.

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Table 1. Effect of Side-Chain Length on Standard Interassociation Equilibrium Constants: DMBVPh(24)/PAMA

polymer	$K_{\mathrm{A}}^{\mathrm{std}}$(predicted)	$K_{\mathrm{A}}^{\mathrm{std}}$(experiment)
PMMA (ref)	54.6	54.6
PEMA	47	54.7
PBMA	37	46
PHMA	40.7	41.1
POMA	38.3	40.5
PDMA	35.1	38.1
PODMA	27.3	27.6

Table 2. Effect of Inert Diluent in Backbone on Standard Interassociation Equilibrium Constants: DMBVPh(24)/EMMA(*x*)

polymer	$K_{\mathrm{A}}^{\mathrm{std}}$(predicted)	$K_{\mathrm{A}}^{\mathrm{std}}$(experiment)
PMMA (ref)	54.6	54.6
EMMA(47)	87.2	77.4
EMMA(38)	91.8	84.5
EMMA(33)	94.5	86.9

Previously,[7] we defined s as a function of chain conformation and employed Wu's analysis[10] to obtain

$$s = \frac{8}{3}\frac{b}{d^2} \tag{4}$$

where b $(= C_\infty\langle l_v\rangle)$ is the Kuhn segment length.

Thus, in eq 3, with the knowledge of the characteristic ratio C_∞, statistical skeletal unit length $\langle l_v\rangle$, and molar volume (to obtain chain diameter d), both s and Γ can be calculated. Using this straightforward approach, the standard equilibrium constants ($K_{\mathrm{A}}^{\mathrm{std}}$) can easily transferred not just within homologous series (e.g., PAMA) but across different polymers as long as the functional groups involved in the hydrogen bonding are the same (e.g., C═O groups in methacrylates and acetates).

Using this hypothesis, we investigate the transferability of $K_{\mathrm{A}}^{\mathrm{std}}$ for blends of DMBVPh(24) with PAMA, EMMA(*x*), EVAc(*x*), and DMBAMA(*x*) (shown in Tables 1–4) (EMMA = ethylene-*co*-methyl methacrylate). Using the experimental value of $K_{\mathrm{A}}^{\mathrm{std}}$ for a reference system in eq 3, we can now predict $K_{\mathrm{A}}^{\mathrm{std}}$ for other blend systems involving similar functional groups. For blends of PAMA, EMMA, and DMBAMA, the employed reference is PMMA, while poly(vinyl acetate) (PVAc) serves as the reference system for EVAc blends. The parameters (C_∞, $\langle l_v\rangle$) required for calculating s and Γ have been previously reported by Wu[13] (we employ experimental values) while diameter d was obtained via the molar volume. Finally, because of the absence of data on copolymer characteristic ratios, we employ simple mixing rules to calculate $s\Gamma$ (eq 3) for EMMA, EVAc, and DMBAMA.[14–16]

Table 3. Effect of Inert Diluent in Backbone on Standard Interassociation Equilibrium Constants: DMBVPh(24)/EVAc(*x*)

polymer	$K_{\mathrm{A}}^{\mathrm{std}}$(predicted)	$K_{\mathrm{A}}^{\mathrm{std}}$(experiment)	$K_{\mathrm{A}}^{\mathrm{std}}$(predicted)-PMMA-ref
PMMA		54.6	54.6
PVAc	80.6	80.6	85.9
EVAc(70)	90.8	92.9	96.7
EVAc(45)	96.3	96.1	102.7
EVAc(25)	99.9	102	106.5
EVAc(18)	100.9	101	107.6

Table 4. Effect of Side-Chain Length on Standard Interassociation Equilibrium Constants: DMBVPh(24)/DMBAMA(*x*)

polymer	$K_{\mathrm{A}}^{\mathrm{std}}$(predicted)	$K_{\mathrm{A}}^{\mathrm{std}}$(experiment)
PMMA (ref)	54.6	54.6
DMBMMA(70)	72.2	74.6
DMBMMA(51)	81.7	78.8
DMBMMA(38)	87.5	80.9
DMBMMA(19)	95.3	83.8
PEMA	46.9	54.7
DMBEMA(28)	88.9	82.1
DMBEMA(18)	94	84.7
DMBPMA(28)	87	74.6
DMBPMA(23)	89.9	74.4
PBMA	37.2	46.1
DMBBMA(33)	82.2	72.1
DMBBMA(24)	87.8	72.6
PDMA	35.4	38.1
DMBDMA(89)	42.5	54.2
DMBDMA(73)	52.7	68.3
DMBDMA(47)	70.2	71.9
DMBDMA(32)	79.8	72.1

For blends of DMBVPh(24) with homologous series of PAMA (Table 1), the predicted values of $K_{\mathrm{A}}^{\mathrm{std}}$ are generally in very good agreement with the experimentally measured interassociation equilibrium constants. Note that the observed differences between predicted and experimental values for PEMA and PBMA blends is probably a result of the inaccuracies in the characteristic ratios employed for the calculations. Despite these discrepancies, our empirical approach accurately predicts the decrease in FGA as alkyl methacrylate side chain length increases. In contrast, Table 2 shows the effect of increased spacing using "inert" CH_2 spacer groups in the backbone between PAMA repeat units. Our approach predicts increase in $K_{\mathrm{A}}^{\mathrm{std}}$ corresponding to an increase in FGA as the wt % of ethylene groups increases. Again, we are able to reproduce the trend and calculated values are in good agreement with experimental values. As stated in the beginning, it has been our intention to develop a universal approach which is valid across different blend systems as long as the functional groups involved in the hydrogen bonding are the same. The results in Table 3 clearly validate our assertion. In step one we used PVAc as reference and predict $K_{\mathrm{A}}^{\mathrm{std}}$ for EVAc blends using eq 3 with remarkable accuracy (column 3). Then taking a step further instead of PVAc, we now employ PMMA as the reference and use eq 3 to predict $K_{\mathrm{A}}^{\mathrm{std}}$ for PVAc and EVAc copolymers (column 4). Clearly, there is very good agreement between predicted and experimental values. This demonstrated the concept of transferability of $K_{\mathrm{A}}^{\mathrm{std}}$ using our approach. Finally, Table 4 lists the predicted and experimental $K_{\mathrm{A}}^{\mathrm{std}}$ values for DMBVPh (24)/PAMA copolymers using dimethylbutadiene (DMB) as "inert" spacer groups for the PAMA copolymers. In this case as discussed earlier, FGA is a combination of two effects: increase in spacing between PAMA repeat units and increase in length of PAMA side chains. Within each series, namely PMMA, PEMA, PBMA, PDMA, our approach correctly predicts[15,16] that $K_{\mathrm{A}}^{\mathrm{std}}$ increases with increase in the number of "inert" DMB groups (or decrease in alkyl methacrylate groups). For example, within DMBMMA (dimethylbutadiene-*co*-methyl methacrylate), predicted $K_{\mathrm{A}}^{\mathrm{std}}$ increases from 54.6 for pure PMMA to 95 for DMBMMA(19) (19 wt % PMMA groups). Similarly for DMBDMA, as wt % of PDMA decreases from 100 to 32% (or DMB wt % increase from 0 to 68%), $K_{\mathrm{A}}^{\mathrm{std}}$ increases from 42.5 to ~80. In contrast, as the length of the PAMA side chain increases, the approach accurately predicts a decrease in $K_{\mathrm{A}}^{\mathrm{std}}$. Thus, $K_{\mathrm{A}}^{\mathrm{std}}$ changes from ~72 for DMBMMA (70) to ~53 for DMBDMA(73). Interestingly, $K_{\mathrm{A}}^{\mathrm{std}}$ is constant (~80) for both DMBBMA(33) and DMBDMA(32) despite a drastic increase in side chain (from PBMA to PDMA), which indicates that the effect of increased side chain length on $K_{\mathrm{A}}^{\mathrm{std}}$ can be stabilized by increasing the backbone spacing. For DMBVPh(24)/DMBAMA copolymer blends, while the predicted values appear to be overestimated by ~10−15% for some blends, in general there is very good agreement between predicted and experimental trends. Overall, using our approach, the transferability of K_A^{std} is remarkable.

In summary, our model permits the transferability of K_A^{std} for the first time across various types of polymer A, as long as the functional group of component A involved in hydrogen bonding is the same. We are currently in the process of validating our approach for more complex systems where the compositions of both components (B and A) are changed by addition of inert comonomers (e.g., DMBVPh(x)/EVAc(y)).

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References and Notes

(1) The systems under consideration all involve strong hydrogen bonds.

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(7) K_A^{std} is the interassociation equilibrium constant K_A at $T = 25$ °C and normalized to a molar volume of $V_B = 100$ cm^3/mol (see refs 1−4).

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(14) Noting that (sb) is dimensioless, we employ the mixing rule $(sb)_{copolymer} = \sum_{i=1}^{n}(s_i b_i)\phi_i$. Finally, $(s\Gamma)_{copolymer} = (sb)_{copolymer}/d_{copolymer}$, where $d_{copolymer}$ is obtained using copolymer molar volume.

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(16) For PDMB, $C_\infty = 7.0$ (ref 14). The double bond in PDMB will hinder rotation around the backbone. For our calculations, $\langle l_v \rangle$ was taken as 1.73, i.e., average of $\langle l_v \rangle = 1.98$ (calculated using $n_v = 3$, no rotation around double bond, n_v = number of statistical segments in a repeat unit) and $\langle l_v \rangle = 1.483$ (calculated using $n_v = 4$, rotation around double bond).

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