Comments & Replies

Comments on "Measurement of the Infinite Dilute Activity Coefficients and Diffusion Coefficients of Water and Straight Chain Alcohols in Cross-Linked Polyvinyl Alcohol by Inverse Gas Chromatography" (Wang, D.; Li, J.; Zeng, C.; Chen, J.; Chen, C. *J. Chem. Eng. Data* 2007, *52*, 368−372)

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In a recently published article, Wang et al. reported a collection of mass fraction activity coefficients γ_w for several solvents in a cross-linked polyvinyl alcohol and in pure polyvinyl alcohol. The values obtained by these authors are exceptionally high for both of the polymers. Solvents can be classified according to their γ_w as follows:[1] good ($\gamma_w < 5$), moderate ($5 < \gamma_w < 10$), and bad solvent ($\gamma_w > 10$). Wang. et al. reported γ_w values around 23 for water in polyvinyl alcohol (see their Table 2). Following the previous classification, water would be considered as a bad solvent for polyvinyl alcohol. This result is illogical because polyvinyl alcohol is known to be one of the few polymers that can be dissolved in water, and therefore, a smaller γ_w would be expected. Palamara et al.,[2] using a gravimetric sorption balance, have published the sorption isotherm for several solvents including water and methanol in polyvinyl alcohol. Their data yield values of the γ_w close to 5.

The unexpected results presented in this manuscript could be due to incorrect calculation of the γ_w. Polyvinyl alcohol is known to be a highly crystalline polymer because the hydroxyl groups are small enough to easily fit into the crystalline structure. Also, because of hydrogen bonding, those crystallites are thermally very stable and have a melting temperature in the range of 180 to 220 °C. Because the experiments were all conducted at or below 150 °C, a semicrystalline structure would be expected. Palamara et al.[2] have reported a crystalline content around 64 % for polyvinyl alcohol. Crystallinity has an important role in sorption because solvents cannot easily penetrate the crystal structure, and sorption takes place only in the amorphous region of the polymer. The γ_w should be corrected for the crystallinity and expressed in terms of the γ_w of the amorphous phase, especially if comparisons are to be made with other polymers. In the manuscript, the authors compare the measured γ_w for the uncross-linked and the cross-linked samples. They are comparing samples that most likely have different amounts of amorphous regions and, therefore, have different sorption capabilities. The correction for crystallinity may explain, also, the big difference between the γ_w of polyvinyl alcohol and that of the cross-linked version. Two polyvinyl alcohol samples, with cross-linking of 4 % and 2 %, the latter one reported by Zeng et al.,[3] were compared with polyvinyl alcohol. The γ_w changes from 23 for polyvinyl alcohol to 176 for a cross-linking content of 2 % and to 353 for 4 % cross-linking. It seems logical that by increasing the degree of cross-linking the crystalline content decreases. If the measured γ_w is divided by the volume fraction of the amorphous region or if in eq 5 w_2 is considered the mass of amorphous polyvinyl alcohol instead of the total mass, more rational numbers may have been observed.

Polyvinyl alcohol is an important polymer for barrier and membrane materials, and a comprehensive collection of thermodynamic and transport data would be necessary for improving the performance of these materials. For this reason, more care needs to be taken when these data are presented in order not to lead to inaccurate conclusions.

Editors Note: The authors did not respond to requests to reply to this comment.

Literature Cited

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