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Comments & Replies

Reply to Comments by J. Román Galdámez on *J. Chem. Eng. Data* 2007, *52*, 368−372

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In his comments on the above paper, Galdámez[1] considers that the infinite dilute activity coefficients for solvents in PVA that we measured are exceptionally high for PVA and cross-linked PVA.

To validate the veracity of our data, we measured the crystallinity of PVA and cross-linked PVA by using wide-angle X-ray diffraction (Rigaku D/Max-2500), to obtain the infinite dilute activity coefficients for water in PVA based on the amorphous regions, and compared these data with the data from Palamara et al.[2] by using a gravimetric sorption balance method.

We prepared the samples of PVA and 4 % cross-linked PVA, and through wide-angle X-ray diffraction (as shown in Figure 1 and Figure 2), we determined that the crystallinity of PVA was 48.3 % and that the crystallinity of 4 % cross-linked PVA was 45.6 %. The crystallinity of PVA changes little after cross-linking.

According to the vapor−liquid equilibria data from the literature[2] in Table 1, the mass fraction infinite dilute activity coefficients (Ω^{∞}) for water in PVA based on the amorphous phase are obtained and listed in Table 2.

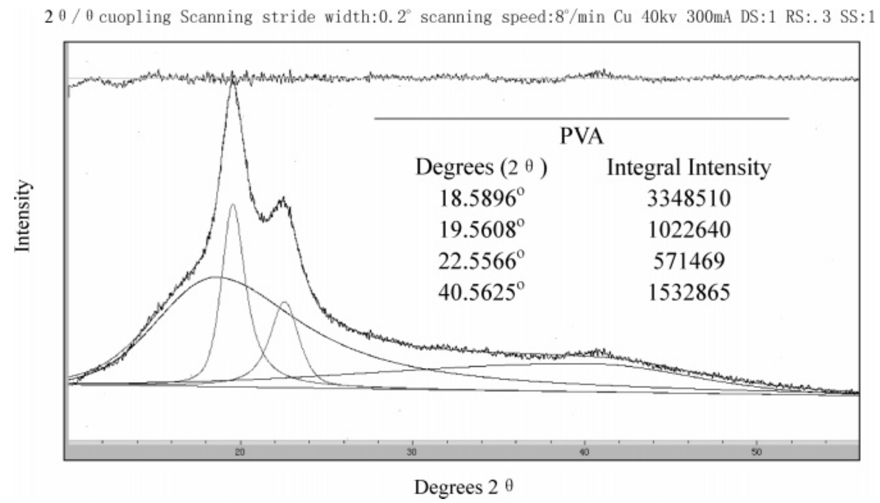

Figure 1. Wide-angle X-ray diffraction about PVA.

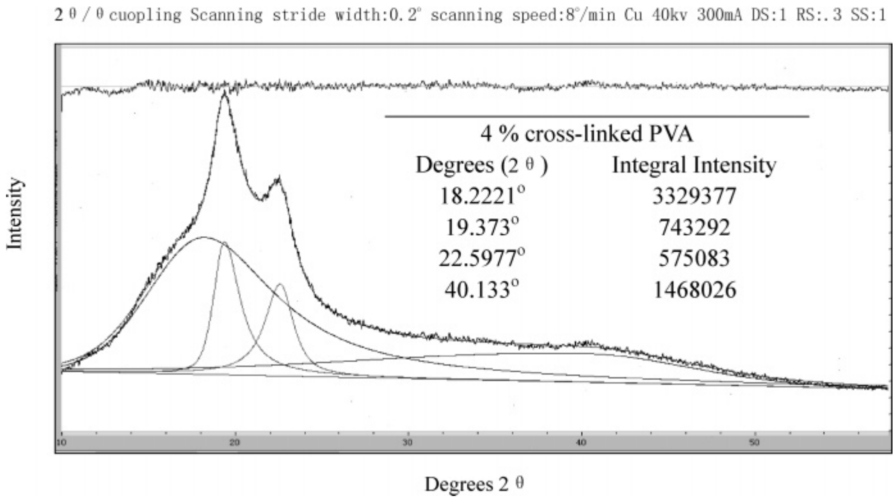

Figure 2. Wide-angle X-ray diffraction about 4 % cross-linked PVA.

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Table 1. VLE Data for Water in the Amorphous Phase of PVA[2]

T (°C)	a_1	ω_{1a}	Ω	T (°C)	a_1	ω_{1a}	Ω
90	0.222	0.0237	9.367089	90	0.909	0.219	4.150685
90	0.224	0.0273	8.205128	100	0.221	0.0228	9.692982
90	0.295	0.0373	7.908847	100	0.49	0.0623	7.865169
90	0.461	0.0523	8.814532	100	0.675	0.112	6.026786
90	0.467	0.0701	6.661912	100	0.849	0.208	4.081731
90	0.701	0.1037	6.759884	110	0.244	0.0222	10.99099
90	0.623	0.117	5.324786	110	0.442	0.0506	8.735178
90	0.891	0.189	4.714286	110	0.621	0.093	6.677419

Table 2. Comparative Ω^∞ for Water in PVA

T (°C)	Ω^∞ (calcd from Palamara et al.'s data, considering crystallinity 36 %)	Ω^∞ (our data, considering crystallinity 48.3 %)	Ω^∞ (our data, without considering crystallinity)
90	9.55		
100	10.54	11.97	23.15[3]
110	12.68	12.33	23.85[3]

In Table 1, a_1 is the activity of water in the amorphous phase of PVA; ω_{1a} is the weight fraction of water in the amorphous phase of PVA; and Ω is the mass fraction activity coefficients of water in the amorphous phase of PVA calculated according to the values of a_1 and ω_{1a}.

Table 2 gives the comparative results of Ω^∞ for water in PVA. From this table, we could find that if we consider the crystallinity of PVA the value of water's Ω^∞ measured by inverse gas chromatography is consistent with the results of Palamara et al. determined using the gravimetric sorption balance method.

Generally, solvent sorption is thought to occur in the amorphous region of polymers, whereas the crystalline region is considered to be impenetrable to solvent. So, adopting Ω^∞ based on the amorphous regions is more logical. However, in some practical industrial processes, it may be hard to differentiate the crystalline and amorphous regions, especially, in the area of membrane separation in which we are interested. When small molecules impenetrate the whole membranes, we could not separate the membranes into the crystal regions and the amorphous regions, and in this case, the Ω^∞ based on the whole polymer seems to be more logical to reflect the macroscopical dissolution behavior of small molecules. So in this case, using Ω^∞ based on the whole polymer would be useful for us to choose the appropriate membrane materials for separating small molecule mixtures.

Editor's Note: A note in the Comment by Galdámez indicates that the author did not respond to requests to reply to the comment; however, the original author, Jiding Li, submitted a late reply.

Literature Cited

(1) Galdámez, J. R. 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.; Chen, J.; Chen, C. *J. Chem. Eng. Data* **2007**, *52*, 368−372). *J. Chem. Eng. Data* **2007**, *52*, 1148.

(2) Palamara, J. E.; Zielinski, J. M.; Hamedi, M.; Duda, J. L.; Danner, R. P. Vapor−liquid equilibria of water, methanol, and methyl acetate in poly (vinyl acetate) and partially and fully hydrolyzed poly (vinyl alcohol). *Macromolecules* **2004**, *37*, 6189−6196.

(3) Zeng, C.; Li, J.; Wang, D.; Chen, T.; Zhao, C.; Chen, C. Infinite Dilute Activity and Diffusion Coefficients in Polymers by Inverse Gas Chromatography. *J. Chem. Eng. Data* **2006**, *51*, 93−98.

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