One of the few ways to accomplish electronic billing to the VA is to enroll as a TriCare provider.
https://health.mil/providers

That's the most direct route, is being in-network and billing directly.

Otherwise, the problem is that Emdeon is the designated clearinghouse for the VA, and their fee, unless it has changed recently, is way too expensive for all except large providers like hospitals.

Knowledgebase
http://kb.barnestorm.biz/KnowledgebaseArticle51450.aspx