化工学报 2007 58 (8): 1917-1925 ISSN: 0438-1157 CN: 11-1946/TQ

传递现象

反相气相色谱法测定小分子溶剂在聚乙烯粒子中的无限稀释扩散系数

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收稿日期 2006-10-8 修回日期 2007-5-25 网络版发布日期 2007-8-3 接受日期

摘要

基于经典线性非平衡色谱过程的矩分析理论，用反相气相色谱法测定了323.15～358.15 K温度范围内二氯甲烷、三氯甲烷、四氯甲烷3种不同相对分子量的同系物小分子及正己烷在聚乙烯粒子中的无限稀释扩散系数。采用聚合物粒子直接填充的色谱柱，考察了温度、同系物小分子分子量及聚乙烯结晶度对扩散系数的影响。实验结果表明，对同一种小分子溶剂/聚乙烯体系，扩散系数均随温度升高而增大。不同相对分子量的同系物小分子在同一种聚乙烯中扩散系数随分子量增加而减小，聚乙烯结晶度增加也会导致扩散系数减小。采用文献中所报道的Krevelen扩散系数预测模型的计算值与实验测量值较为吻合，表明本文所采用的以聚合物粒子直接填充色谱柱的反相气相色谱扩散分析具有一定的可靠性。

关键词

无限稀释扩散系数 小分子溶剂 聚乙烯粒子 反相气相色谱

分类号

Measurement of infinite dilution diffusion coefficients of small molecule solvents in nascent polyethylene particles by inverse gas chromatography

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Abstract

Based on the classical theory of linear and non-equilibrium chromatography process, the infinite dilution diffusion coefficients of dichloromethane, tri-chloromethane, tetra-chloromethane and n-hexane in nascent polyethylene particles were measured in the temperature range from 323.15 K to 358.15 K with inverse gas chromatography (IGC). Polyethylene particles, as obtained from the polymerization reactor, were directly used to prepare packed columns without any change of the polymer morphology. The effects of diffusion temperature, molecular weight of different solvents and polyethylene crystallinity on diffusivity were investigated. It was shown by the IGC results that the diffusion coefficients increased with rising temperature for a particular polymer/solvent system, while decreased with increasing molecular weight of diffusing solvent for homologue solvents, such as dichloromethane, tri-chloromethane and tetra-chloromethane. The crystallinity of semicrystalline polyethylene also affected the diffusion coefficients significantly in the way that higher crystallinity corresponded to lower diffusion coefficients for both dichloromethane and n-hexane. The measured diffusion coefficients were compared with model predicted values and good agreement was found, indicating the reported IGC method in this work had good reliability.

Key words

infinite dilution diffusion coefficient small molecule solvent polyethylene particle inverse gas chromatography

DOI:

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