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研究论文

丙三醇浓溶液T_g附近协同松弛的量热研究

高才[1], 王铁军[1], 周国燕[2], 华泽钊[2]

1. 合肥工业大学机械与汽车工程学院, 合肥 230009;
2. 上海理工大学低温生物研究所, 上海 200093

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摘要

利用差示扫描量热法测量了丙三醇水溶液Tg前后的比热容. 通过曲线拟合获得AGF模型参数. 研究结果表明, 该模型很好地预测了(T_g+20 K)以下体系的结构松弛时间. 协同重排活化能($\Delta\mu'$)和协同重排域尺寸(z^*)的分析结果表明, 只有选择比聚合物大得多的某一协同重排位形数, 用AGF方法得到的z^*才具有物理意义. 作为材料常数的$\Delta\mu'$随体系水含量的增加而逐渐降低. 用Donth方法得到的丙三醇水溶液的协同重排域长度尺度(ξ_{CRR})随着水含量的增加逐渐降低, 且其变化趋势可与$\Delta\mu'$的分析结果相符. 但用AGF方法和Donth方法得到的协同重排域尺寸不能统一.

关键词 协同松弛 丙三醇 水溶液 差示扫描量热法

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Calorimetric Studies on Cooperative Relaxation Near T_g for a Series of Glycerol Aqueous Solutions with High Concentrations

GAO Cai[1]*, WANG Tie-Jun[1], ZHOU Guo-Yan[2], HUA Ze-Zhao[2]

1. School of Mechanical and Automotive Engineering, Hefei University of Technology, Hefei 230009, China;
2. Institute of Cryobiology, University of Shanghai for Science and Technology, Shanghai 200093, China

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Abstract In order to examine the validity of entropically based nonlinear Adam-Gibbs equation (AGF) on the describing of cooperative relaxation of H-bond molecular liquid, differential scanning calorimetry(DSC) was employed to obtain the specific heat capacities of glycerol aqueous solutions in the temperature range of 118—218 K. Curve fitting technology was used to obtain the AGF model parameters. The results indicate that AGF formula can be used to predict the relaxation time below (T_g+20 K). The temperature-invariant activation energies ($\Delta\mu'$) and the sizes of cooperatively rearranging region(z^*) were analyzed *via* AGF model and Johari's method. Physically reasonable z^* can only be obtained when larger values of configuration numbers(W^*) were chosen. The values of $\Delta\mu'$ decreased with increasing water content in the glass. The length scales of the cooperative rearranging region(ξ_{CRR}) were also estimated from the temperature fluctuation theory proposed by Donth. It was found that the ξ_{CRR} decreased from 3.01 to 2.06 nm when the fraction of glycerol decreased from 1 to 0.6 in the solutions. The values of z^* obtained by using Johari's methods is 3.47 for glycerol, which is significantly less than the number of molecules estimated by Donth' method(583) in the CRR.

Key words Cooperative relaxation; Glycerol; Aqueous solution; Differential scanning calorimetry

通讯作者:
高才 gao_cai@hotmail.com
作者个人主页: 高才[1]; 王铁军[1]; 周国燕[2]; 华泽钊[2]