Kinetic Analysis of Radiation-Initiated Copolymerization Reactions of Water-Soluble Vinyl Monomers with Cellulose

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Synopsis

A kinetic analysis of the radiation-initiated copolymerization reactions of 2-hydroxyethyl methacrylate (HEMA), hydroxypropyl methacrylate (HPMA), and methacrylic acid (MAA) from water, methanol (MeOH), N,N-dimethylformamide (DMF), dimethylsulfoxide (DMSO), and combinations of these solvents with irradiated fibrous cellulose I and II was made. The maximum extent of copolymerization of HEMA and HPMA with irradiated cellulose occurred from water solutions. When organic solvents were added to the water solution, while the concentration of monomer was kept constant, the extent of copolymerization decreased. The maximum extent of copolymerization of MAA with irradiated cellulose occurred from mixtures of MeOH (15–30 vol-%) and water (85–70 vol-%) solutions rather than from water. After initiation of the copolymerization reactions, they were apparently diffusion controlled and exhibited second-order kinetics. The relative concentrations of grafted polymer and homopolymer formed with irradiated cellulose from aqueous solutions depended primarily on the concentration of water in the solutions. From MeOH (60 vol-% or less)–water (40 vol-% or more) solutions, about 60% of poly(MAA) formed was apparently grafted polymer; from solutions containing less water, the fraction of grafted polymer decreased to about 40%.

INTRODUCTION

Free radical-initiated copolymerization reactions of water-soluble vinyl monomers and monomers which contain polar groups with cellulose have been reported to a limited extent.[1] Generally, these reactions were initiated by redox systems or heat. It has been shown that radiation-initiated reactions of monomers with fibrous cellulose, particularly postirradiation reactions, make possible selective and controlled changes in the properties and morphology of the fibrous cellulose–polyvinyl copolymers.[2,3] The use of water-soluble monomers and monomers which contain polar groups would also offer the possibility of changing the surface properties of the

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fibrous copolymers to increase ion exchange capacity and hydrophilicity. This could lead to increased soil-release properties of cellulosic textile products, as we have reported.[4]

In this report, a kinetic analysis of the copolymerization reactions of methacrylic acid, 2-hydroxyethyl methacrylate, and hydroxypropyl methacrylate from aqueous solutions with irradiated cotton fibers is presented. Reactions of these monomers with irradiated cotton fibers, both cellulose lattice types I and II, are considered.

EXPERIMENTAL

Materials

Cotton fibers of the Deltapine variety were purified in the usual manner.[5] The cotton fibers were washed with distilled water to remove the sodium hydroxide, soured with dilute acetic acid, and then neutralized with dilute ammonium hydroxide solution. Finally, the cotton fibers were washed with distilled water and air dried at room temperature. The purified cotton fibers, after conditioning at 21°C and 65% RH, had a moisture content of about 7% and a viscosity-average molecular weight of 700,000[6] and gave a typical cellulose I type of x-ray diffractogram.[7]

Samples of these purified cotton fibers were mercerized by immersion in 23% sodium hydroxide solution at room temperature for 15 min, then washed free of sodium hydroxide as described above, and air dried at room temperature.[8] These treated samples gave a typical x-ray diffractogram for mercerized cellulose, that is, cellulose II.[7]

The monomers [2-hydroxyethyl methacrylate (HEMA), 93%; hydroxypropyl methacrylate (HPMA), 94.5%; methacrylic acid (MAA), 98% purity] were obtained from commercial sources. The impurities in HEMA and HPMA were dimethacrylates and/or methacrylic acid. For purposes of the calculations, 100% purity was assumed. Immediately before use, the monomers were passed through columns of activated alumina (grade F-20, 80-200 mesh, obtained from Alcoa Chemicals) to remove inhibitors (hydroquinone type) of polymerization. The solvents [methanol (MeOH), N,N-dimethylformamide (DMF), and dimethyl sulfoxide (DMSO)] were reagent grade. Distilled water was used to prepare the solutions.

Methods

The SRRL ^{60}Co source was used.[9] The dose rate, determined by ferrous–ferric dosimetry,[10] was about 1.15 Mrad/hr. Samples of purified cotton fibers (1.5 g) were dried over P_2O_5 under vacuum at 40°C for 16 hr and then irradiated at ambient temperature (about 24°C) in an atmosphere of dry nitrogen to the desired dosage.

After irradiation, samples of the irradiated cotton fibers (1.5 g) were immersed in monomer solutions (50 ml) at 25°C. Vacuum was applied to the solutions which were then purged with nitrogen (oxygen free) for 2 min

prior to addition of the fibers. After addition of the fibers, vacuum was again applied briefly to the solutions to minimize the time required for the penetration of the solution into the macrostructure of the fibers; then the copolymerization reaction was allowed to proceed for the desired time under a positive nitrogen pressure. The grafted fibers were washed in distilled water, followed by washing in MeOH–water solution (50–50 vol-%) at 25°C. After a final wash with distilled water, the fibers were dried overnight in a vacuum oven at 40°C. These fibers were conditioned at 21°C and 65% RH and weighed. The increase in weight (% add-on) was recorded as grafted polymer and homopolymer. Some of these fibers were further extracted, three consecutive times, by immersing them in boiling MeOH–water solution (50–50 vol-%) for 7 hr. After each extraction the fibers were washed with methanol and then water, dried, and weighed. The increase in weight of the fibers, after the third extraction, was considered to represent grafted polymer.

RESULTS AND DISCUSSION

The effects of type of solvent on extent of copolymerization of HPMA with irradiated cellulose I are shown in Figure 1. The maximum extent of copolymerization of HPMA with irradiated cellulose occurred in HPMA–water solution. When organic solvents were added to the water solution, while the concentration of HPMA in the solution was kept constant, the
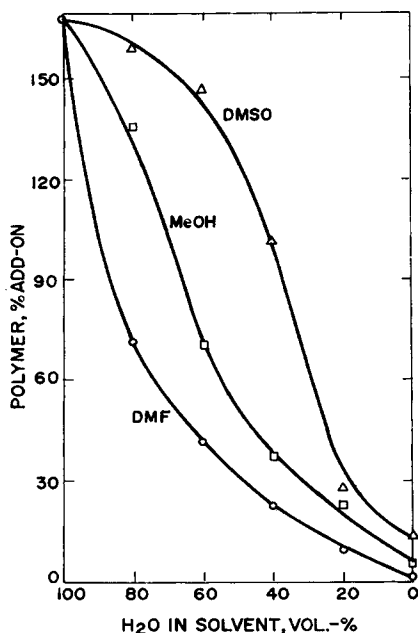

Fig. 1. Effects of type of solvent on extent of copolymerization HPMA with irradiated cellulose I at 25°C. Dosage 1 Mrad; reaction time 30 min; 15 vol-% HPMA in solvent.

extent of copolymerization decreased.   The effects of solvent on polymer
add-on were DMF > MeOH > DMSO.   The maximum rates of decrease
in polymer add-on occurred in water solutions containing 0–20 vol-% DMF,
30–60 vol-% MeOH, and 60–80 vol-% DMSO.   The compositions of the
latter two solvents are approximately those at which the solvents (monomer
absent) exhibit maximum viscosity.   The configuration of the growing
polymer chain, and hence the rate of the copolymerization reaction, could
change with a change in viscosity of the solvent.   Copolymerization from
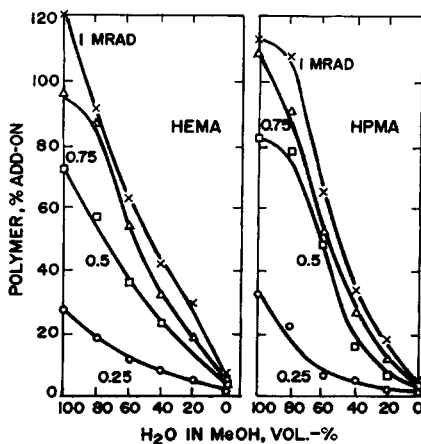DMF, MeOH, and DMSO was very low, indicating that either monomer

Fig. 2. Effects of dosage on extent of copolymerization of HEMA and HPMA in MeOH-
water solutions with irradiated cellulose I at 25°C.   Reaction time 30 min; 6 vol-%
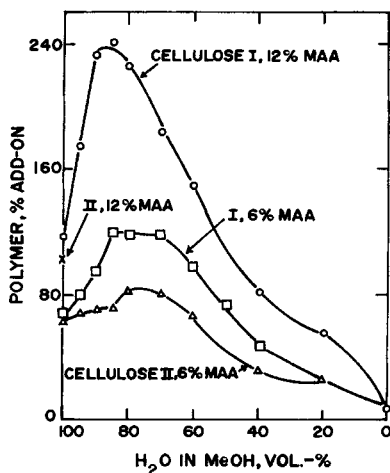monomer in solvent.

Fig. 3. Effects of concentration of MAA in MeOH–water solutions on extent of copoly-
merization with irradiated cellulose I and II at 25°C. Dosage 1 Mrad; reaction time
30 min.

in these solvents did not readily come into contact with the free-radical sites, the radical sites were more rapidly scavenged by these solvents than by water, or the solvents restricted chain propagation.

The effects of radiation dosage on the extent of copolymerization of HEMA or HPMA in MeOH–water solutions with irradiated cellulose I are shown in Figure 2. The extent of copolymerization from MeOH–water
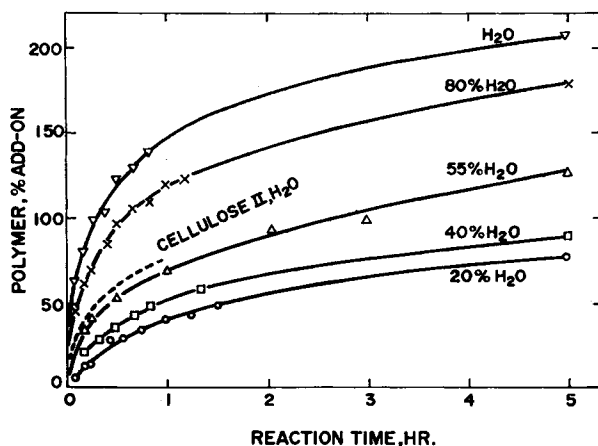

Fig. 4. Effects of reaction time on extent of graft copolymerization of HEMA in MeOH–water solutions with irradiated cellulose I and II at 25°C. Dosage 1 Mrad; 6 vol-% HEMA in solvent.
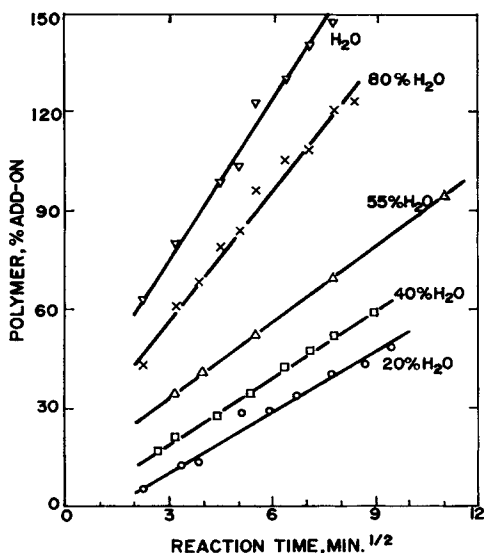

Fig. 5. Effects of reaction time on extent of graft copolymerization of HEMA in MeOH–water solutions with irradiated cellulose I at 25°C. Dosage 1 Mrad; 6 vol-% HEMA in solvent.

solutions increased with an increase in radiation dosage and was a maximum in water solutions.

The effects of concentration of MAA in MeOH–water solutions on the extent of copolymerization with irradiated cellulose I and II are shown in
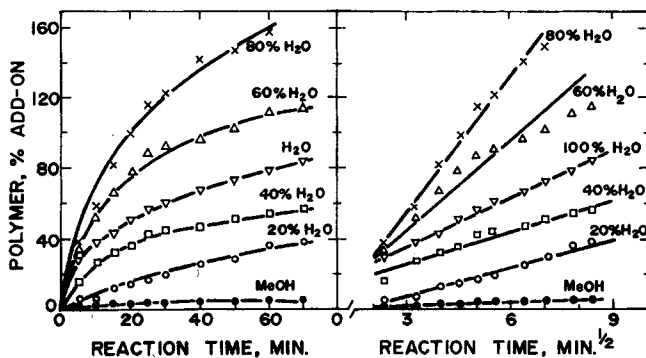

Fig. 6. Effects of reaction time on extent of graft copolymerization of MAA in MeOH–water solutions with irradiated cellulose I at 25°C. Dosage 1 Mrad; 6 vol-% MAA in solvent.
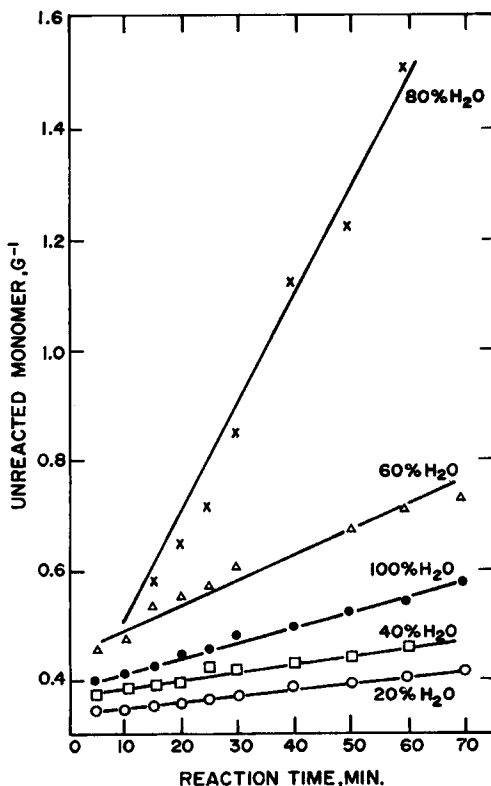

Fig. 7. Effects of reaction time on extent of the reaction of MAA in MeOH–water solutions with irradiated cellulose I at 25°C. Dosage 1 Mrad; 6 vol-% MAA in solvent.
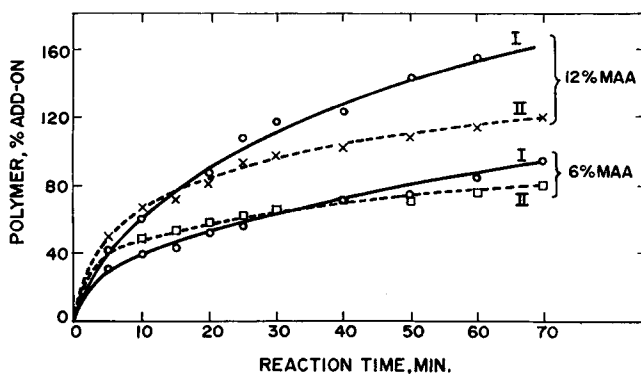
Fig. 8. Effects of reaction time on extent of graft copolymerization of MAA in water with irradiated cellulose I and II at 25°C.   Dosage 1 Mrad.
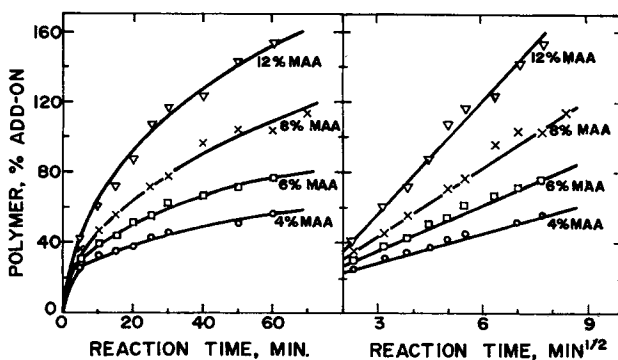

Fig. 9. Effects of concentration of MAA in water on the extent of graft copolymerization with irradiated cellulose I at 25°C.   Dosage 1 Mrad.

Figure 3.   As the concentration of MAA increased, the extent of copolymerization increased and was greater with irradiated cellulose I than with irradiated cellulose II.   The maximum extent of copolymerization of MAA with irradiated cellulose occurred from MeOH (15–30 vol-%)–water (85–70 vol-%) solutions rather than from water, as was observed for HEMA and HPMA.   It has been reported that poly(MAA) in MeOH (20–30 vol-%)–water (80–70 vol-%) solutions exhibited a minimum viscosity.   The viscosity of the solutions was dependent on the molecular weight of the poly(MAA) and was greater in MeOH than in water solutions.[11]   This indicates that addition of MeOH to aqueous solutions of poly(MAA) leads to breakdown of the compact structures reportedly stabilized by hydrophobic interactions[11,12] (hydrophobic interactions are reportedly present in solutions of poly(HEMA)[13]) and to unfolding of the macromolecule.   It is interesting to note that the maximum extent of copolymerization of MAA with irradiated cellulose was obtained in MeOH–water solution in which poly(MAA) exhibited maximum viscosity.   In these postirradiation co-
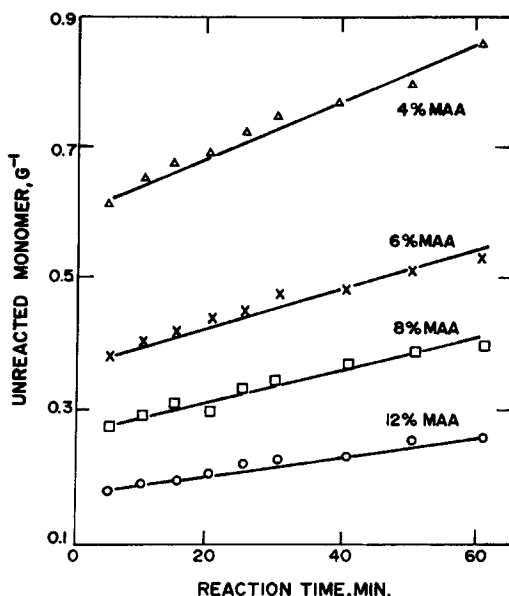
Fig. 10. Effects of reaction time on the extent of the reaction of MAA in water with irradiated cellulose I at 25°C. Dosage 1 Mrad.

polymerization reactions, it is assumed that the reactions occurred primarily within the macrostructure of the irradiated cellulosic fibers. Then, if viscosity effects observed in homogeneous media apply to the heterogeneous system under investigation, the effects observed cannot be explained solely by the Trommsdorff-type effect.[14] However, changes in the viscosity of solutions of poly(MAA) may result from the formation of graft copolymers and homopolymers in the cellulosic matrix which may be partially soluble in solution entrapped in the matrix. A combination of several effects may explain the observed result.

The effects of reaction time on the extent of graft copolymerization of HEMA in MeOH–water solutions with irradiated cellulose I and II are shown in Figure 4. In water, almost all of the HEMA was polymerized after 5 hr. The initial rate of copolymerization was the highest in HEMA–water solutions and decreased as MeOH was added to the solutions. The extent of copolymerization of HEMA in water solutions with irradiated cellulose I was about twice that with irradiated cellulose II, under similar experimental conditions. A linear relationship between extent of copolymerization and the square root of reaction time, up to about 1.5 hr (see Fig. 5), was observed. These relationships did not extrapolate to zero conditions, probably because of the heterogeneous nature of the reaction media and the time required for the solutions to penetrate the cellulosic matrix to the free-radical sites.

The effects of reaction time on the extent of graft copolymerization of MAA in MeOH–water solutions with irradiated cellulose I are shown in
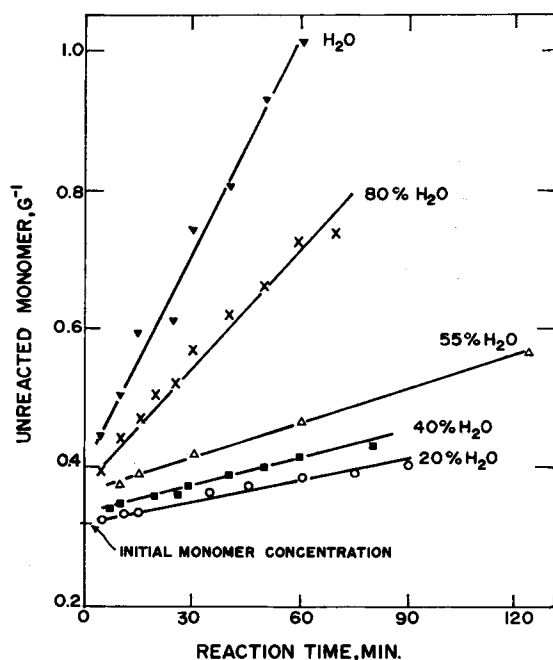
Fig. 11. Effects of reaction time on the extent of the reaction of HEMA in MeOH–water solutions with irradiated cellulose I at 25°C.   Dosage 1 Mrad;   6 vol-% HEMA in solvent.

Figure 6.   The initial rate of copolymerization increased with the initial addition of MeOH to the solutions and then decreased on further addition of MeOH (compare with Fig. 3).   A diffusion-controlled reaction was probably indicated by the linear relationship between the extent of copolymerization and the square root of the reaction time.   The linear relationship between the reciprocal of the concentration of unreacted MAA, $(a - x)^{-1}$, in MeOH–water solutions with reaction time is shown in Figure 7, indicating second-order kinetics with respect to monomer.

The effects of reaction time and concentration of MAA in water solutions on the extent of graft copolymerization with irradiated cellulose I and II are shown in Figures 8, 9, and 10.   The initial rate of the polymerization reaction of MAA with irradiated cellulose II was greater than that with irradiated cellulose I;   however, after 15–30 min of reaction, the extent of copolymerization was greater with cellulose I than with cellulose II.   It has been shown that the concentration of long-lived free-radical sites formed at a given dosage in irradiated cellulose I is greater than that in irradiated cellulose II.[15]   Also, the extent of scavenging of free radicals by water is greater in irradiated cellulose II than in the more crystalline irradiated cellulose I.[16]   Considering these factors, the reactions (see Fig. 8) could be partially explained.   The extent of graft copolymerization increased with increased concentration of MAA.   These reactions were apparently diffu-
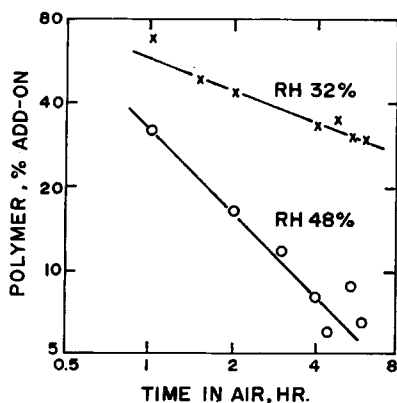
Fig. 12. Effects of water vapor, air, and exposure time of irradiated cellulose I on the extent of graft copolymerization of MAA in water at 25°C. Dosage 1 Mrad; 6 vol-% MAA in water; reaction time 30 min.

sion controlled (see Fig. 9); second-order kinetics were also indicated (see Fig. 10).

The reactions of HEMA in MeOH–water solutions with irradiated cellulose I followed similar kinetics as shown in Figure 11.

The relative concentrations of grafted polymer and homopolymer formed with irradiated cellulose from aqueous solutions depended primarily on the concentration of water in the solutions and to a much lesser extent on the polymer add-on, cellulose lattice type, and initial concentration of monomer. For example, cellulose–poly(MAA) copolymers, prepared by copolymerization of MAA in MeOH–water solutions with irradiated cellulose I, were examined. From MeOH (60 vol-% or less)–water (40 vol-% or more) solutions, about 60% of the polymer formed was grafted polymer (for definition, see Methods); from solutions containing less water, the fraction of grafted polymer decreased to about 40% of the polymer formed from MeOH solutions. When the initial concentration of monomer in the solution was increased, there was an increase in the polymer formed under given experimental conditions; however, there tended to be a decrease in the relative concentration of grafted polymer. These results could be explained on the basis of chain transfer reactions possible in postirradiation reactions of cellulose with monomer solutions, as previously discussed.[17] Apparently, the amount of polymer formed and the cellulose lattice type did not significantly affect the relative concentration of grafted polymer in the polymer formed in these systems.

The kinetic analysis of these copolymerization reactions with irradiated cellulose is complicated by the ease with which the free-radical sites of the irradiated cellulose molecule may be scavenged. In effect, the free radicals may be scavenged by the solutions, or even by water vapor, without initiating copolymerization reactions. We have reported the use of electron spin resonance spectroscopy to determine the extent of scavenging of

free radicals by water vapor and solutions.[18]   The effects of exposure of dried, irradiated cellulose I to air-containing water vapor on the extent of copolymerization of MAA in water are shown in Figure 12.   The yield of copolymer, P, is related to the time of exposure, t, in air at different RH, as follows:

$$P = kt^n$$

where n is dependent on the concentration of water vapor, as expressed by RH.   Under these experimental conditions, at 32% RH at 25°C, $n = -0.33$, and at 48% RH, $n = -1$.

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