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Radiation-induced decomposition of anion exchange resins

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ABSTRACT

Radiation-induced degradation of the strongly basic anion exchange resin Amberlite™ IRA400 in NO_3^-, Cl^- and OH^- forms has been studied. The research focused on the formation of molecular hydrogen in the gamma-radiolysis of water slurries of these quaternary ammonium resins with varying water content. Extended studies with various electron scavengers (NO_3^-, N_2O and O_2) prove an important role of e^-_{solv} in the formation of H_2 from these resins. An excess production of H_2 in these systems at about 85% water weight fraction was found to be due to trimethylamine, dimethylamine and other compounds that leach from the resin to the aqueous phase. Irradiations with 5 MeV ^{4}He ions were performed to simulate the effects of α-particles.

1. Introduction

For several past decades ion exchange resins have served the needs of the nuclear industry in nuclear fuel reprocessing, radioisotope separation, waste management and removal of the radionuclides from reactor coolants [1]. Although they are designed to perform in the harsh conditions found in the nuclear industry, synthetic ion exchange resins, as any other organic polymers, undergo radiation-induced chemical decomposition. The radiation effects on ion exchange resins are manifested in numerous ways and very often lead to undesirable changes in the functional performance of the polymer. For example, continuous exposure of resins to ionizing radiation leads to the destruction of the functional groups available for the ion exchange [2]. The released gaseous products may disturb the individual layers of the ion exchanger column and reduce its separating performance [3]. Products due to radiolysis may continue to react with their environment thus interfering with the functionality of the resin or giving rise to the dangerous radioactive compounds (like HI derived from radioiodine) [4]. Therefore, the recognition and investigation of the impact of ionizing radiation on ion exchange resins is important to ensure safe and reliable operation of these systems.

The vast majority of the studies conducted on ion exchange resins concerns radiation-induced changes in their general physico-chemical properties such as: total exchange capacity, water retention capacity, salt-splitting capacity, crushing strength, weight loss and pH [2–6]. These parameters are directly related to the functional performance of the exchanger. However, the radiation chemistry of ion exchange resins has not received equally much attention. A dated review article by Pillay refers to studies on ion exchange resins that mostly concern the gas evolution during radiolysis of resins or the release of the water-soluble products like amines or ammonia [2,3]. A limited understanding of the radiation-induced decomposition mechanism of resins has been achieved in these works. In particular, the importance of deamination reaction in the radiolysis of quaternary ammonium resins has been shown [7–10].

Among more recent reports on the subject is a detailed study of poly(4-vinylpyridine) based ion exchange resins [11]. The radiation-chemical yields of gaseous products were determined in this work and a variety of spectroscopic methods were employed to follow the changes in resins upon irradiation. A good example of the science-based design of new bifunctional anion exchange resins is described in the paper by Marsh et al. [12]. The performance for the extraction of Pu(IV) is increased by the modification of existing commercial Reillex™ polymer by attaching a second anion-exchange group through a spacer. Work by Nogami et al. discusses the comparison of radiolytic behavior between pyridine and quaternary ammonium type anion exchange resins [13]. They find important changes in the resin stability in different media. For instance, pyridine-based polymers decompose faster in nitric acid environments than in hydrochloric acid. In contrast, quaternary ammonium type resins are more stable in nitric acid than in hydrochloric acid.

A variety of technical issues arise from the production of H_2 and/or O_2 in the radiolysis of resins because of the serious safety concerns related to their flammability and explosion potential [14–16]. Since most separation processes take place in aqueous environments, the radiolytic decomposition of water itself and possible interaction of reactive species produced in radiolysis of

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water and resin must be taken into account. These systems are heterogeneous and virtually impossible to predict with respect to their radiation stability because of the lack of suitable experimental studies. These systems are not fully safe without a detailed knowledge of the radiation chemistry of the organic ion resins. Experimental studies of these complex systems may help to fully understand the effects of radiation on the resins used in the conditions encountered in the nuclear industry.

The radiation-induced decomposition of quaternary ammonium resin represented by the Amberlite™ IRA400 has been investigated in this work. Amberlite™ IRA400 is a strongly basic anion exchange resin based on polystyrene divinylbenzene copolymer. Functionality of the resin is due to the quaternary ammonium moiety. The chemical structure of the chloride form of the resin is shown schematically on Fig. 1. In fact, Amberlite™ IRA400 (trademark of Rohm&Haas Company) belongs to a large family of quaternary ammonium ion exchange resins and, depending on the manufacturer and the country of origin, is known as Dowex™ 1 X-8 (Dow Chemical Company), AG1 X-8 (Bio-Rad Laboratories USA), Deacidite FF (UK), AV-17 (former USSR), Diaion SA100 (Japan), GS-300 and A-23 (India). Although the exact chemical structure and the bead size distribution of these resins are different because of obvious reasons, all of them are built on polystyrene divinylbenzene matrix and the quaternary ammonium group is responsible for their separation functionality. Hence, one can expect the radiation chemistry of these materials to be essentially the same.

In the present work, three different anion forms of Amberlite™ IRA400 resin (nitrate, chloride and hydroxide) have been examined and the effect of the anion has been evaluated. Special emphasis is given to the yield of H_2 in the γ-radiolysis of water slurries of these resins with different amounts of adsorbed water. Heavy ion irradiations with 5 MeV ^{4}He ions were conducted in order to mimic α-particle radiolysis. Conclusive identification of the precursor to H_2 in the radiolysis of Amberlite™ IRA400 resins has been accomplished.

2. Experimental section

2.1. Materials

Amberlite™ IRA400 chloride (AmbCl) and Amberlite™ IRA400 hydroxide (AmbOH) were obtained from Sigma Aldrich and Supelco. Poly(4-vinylpyridine) ammonium chloride Reillex™ HPQ was purchased from Sigma Aldrich. These resins were washed with small amounts of deionized water several times, filtered and dried under vacuum at 30 °C for at least 3 days until weight loss of the samples became negligible (less than 0.1%). Although they are exposed to the vacuum for more than 70 h, the resins do not necessarily become “absolutely dry”, i.e. do not contain any water at all. Some residual water can still be retained within the polymer structure due to strongly polar quaternary ammonium groups.

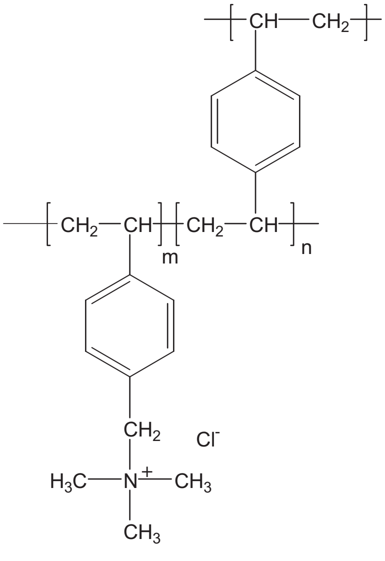


Fig. 1. Chemical structure of Amberlite™ IRA400 chloride resin.

The nitrate form of Amberlite™ IRA400 ($AmbNO_3$) was prepared by anion exchange in AmbCl using aluminum nitrate $Al(NO_3)_3$ [11]. Five grams of AmbCl deposited on a glass filter were treated with an aqueous 0.1 M solution of aluminum nitrate. The flow rate through the filter was about 2 ml/min and 600 ml of nitrate solution were eventually used. The final effluent did not contain any chloride traces since no reaction with Ag^+ was observed. The obtained resin was rinsed three times with water, filtered and dried under vacuum at 30 °C.

A relatively low drying temperature was used to avoid thermal decomposition of the resins, especially the AmbOH. Strong fish-like odor is released by the AmbOH revealing chemical instability of this resin. No difference in appearance of the samples after drying was noticed, with the exception of the hydroxide form of the resin, which turns from a light yellow color to dark brown under vacuum. The pH of the water extracts from nitrate and chloride forms is slightly acidic or neutral (pH = 5–7), whereas the extract from the hydroxide form is basic (pH = 9–10).

2.2. Water loading

The resins were examined under a wide range of water loading. The vacuum oven conditions discussed above represented the “dry” environment. Two different relative humidity chambers were employed to load specific amounts of water. Magnesium nitrate salt slush was used to create a relative humidity of 53% and the highest relative humidity (~100%) was achieved with water only [17]. Purified samples were kept under vacuum, weighed, and then placed into the constant humidity chambers at 23 °C. The resins were kept in the chambers until their weigh remained constant. About 5 days were necessary to achieve equilibrium for 1 g samples. All the resin samples with higher water content were prepared by direct mixing of the dry resin and appropriate amount of water.

2.3. Irradiations

γ-Radiolysis was carried out using a Shepherd 109–68 ^{60}Co source at the Radiation Laboratory of the University of Notre Dame. The dose rate was 63.1 Gy/min as estimated using the Fricke dosimeter [18]. Total energy absorption by the sample was estimated from the combined weight of resin and water. This approach is justified since the electron densities of the resin and water differ by not more than by 5%. Typically, total sample weights were between 1 and 2 g. Radiolysis of all samples was performed under inert argon atmosphere.

The heavy ion irradiations were performed using the 10 MV FN Tandem Van de Graaff accelerator at the Nuclear Structure Laboratory located in the University of Notre Dame Physics Department. Accelerated ^{4}He ions of 5 MeV energy incident to the resin samples were generated. The window assembly as well as the radiation procedure are the same as reported earlier [19,20]. Energy loss of the helium ions in passing through all the windows was determined from a standard stopping power compilation [21]. The samples were irradiated with completely stripped ions at a charge beam current of about 1.5 nA. Total energy deposition was obtained from the product of the integrated beam current and the ion energy incident to the resin sample. The dosimetry for the dried resins was performed based on the total energy deposition in the local volume exposed to the beam. Energy deposition in both the water and resin is used for dosimetry in the slurries since the samples were mixed thoroughly using an external magnetic stirrer. Doses varied up to 500 kGy. The sample cell was made of quartz with a thin mica window of about 5.0 mg/cm^2 attached to the front for the beam entrance. The cell had an inlet and outlet ports designed for purging the sample before and after irradiation. Total volume of the slurries was about 5 ml.

2.4. H_2 analysis

An inline technique was employed to determine the H_2 production in radiolysis of resin/water mixtures. Gas chromatographic analysis was performed using a SRI 8610 apparatus equipped with a thermal conductivity detector. The chromatographic column was a 6.4 mm diameter 13X molecular sieve 3 m long, maintained at 40 °C. The irradiation cell was made from a quartz cuvette. The sample was degassed with ultra-high purity argon for 10 min at room temperature before irradiation. Calibration was performed by injection of pure H_2 gas at normal conditions.

In few cases, samples for γ-radiolysis were placed in Pyrex tubes (diameter ~1 cm, length ~10 cm), purged with argon for 10 min and flame sealed. Total sample weights were typically about 1 g. Following irradiation, each tube was broken in the inlet line of the gas chromatograph. The estimated error in gas measurements was about 10% and is mainly due to partial adsorption of gases by the resins. The relative changes in H_2 yields are greater than the errors in measurement.

2.5. Ion chromatography

Quantitative analysis of amines leached from resins into the water was performed using a Dionex® 500 ion chromatograph. The system consists of a 25 µl sample loop, a CS12A (4 mm × 250 mm) cation-separating analytical column, a cation self-regenerating suppressor (CSRS ULTRA) operating at 100 mA, a suppressed conductivity detector (CD25) and a Dionex AS40 autosampler. Commercial Chromeleon® software was used to control the operation of the device and also to perform data analysis. A 0.02 M aqueous solution of methanesulfonic acid was employed as eluent, the flow rate was 1.5 ml/min. Under these conditions the retention times were about: 3.16 min for NH_4^+, 3.25 min for $CH_3NH_3^+$, 3.54 min for $(CH_3)_2NH_2^+$ and 4.5 min for $(CH_3)_3NH^+$ cations. Aqueous solutions of NH_4Cl, CH_3NH_3Cl, $(CH_3)_2NH_2Cl$ and of $(CH_3)_3NHCl$ in the concentration range between 25 and 100 µM were used for calibration.

2.6. Spectroscopic analysis

Diffuse reflectance infrared Fourier transform spectroscopy (DRIFT) was performed using a Bruker Vertex 70 FT-IR spectrometer with a resolution 4 cm^{-1} and 512 scans in the range of 400–4000 cm^{-1}. Unfortunately, the resin beads in their original size could not be studied with this reflective spectroscopic technique because of the loss of light due to scattering. Therefore, the resin samples were ground manually and the fraction of the finest powder of smaller than 25 mesh size was collected. This powder was later dried under vacuum as described for the resin beads. Dry powder as well as its mixtures with water were then irradiated in the degassed, sealed tubes with γ-rays to doses up to 0.3 MGy. The aqueous slurries were then dried under vacuum before analysis. Irradiated and dried samples were mixed with KBr powder, so that the weight fraction of polymer was about 5%. These mixtures were then analyzed using DRIFT spectroscopy.

3. Results and discussion

3.1. Water loading and H_2 production

Radiation yields of H_2 were first determined with the dry resins so they could be compared to the effects due to the presence of added water. Great care was taken in drying the resins so they would not thermally degrade. Unfortunately, the relatively mild drying technique probably never completely dried the resins, which retained absorbed water. This small amount of residual water is not significant in determining the amount of absorbed water from the constant humidity chambers, but it could have an effect on the radiation-chemical yield. The only way to determine how much the residual water affects the radiation chemistry is to completely dry the resins, which would probably lead to their decomposition and thereby giving results not representation of the resin. Several drying techniques were used until reproducible data were obtained for the dry compounds. The yields of H_2 in the γ-radiolysis were found to be 0.07, 0.08, and 0.044 molecules/100 eV for the Cl^-, OH^-, and NO_3^- forms of the resin, respectively. (Radiation-chemical yields are given here in the traditional unit of molecules of product/100 eV of energy absorbed, 1 molecule/100 eV = 0.1 µmol/J.) These yields are relatively low and comparable with H_2 yields typically found with aromatic compounds [22]. The NO_3^- form of the resin shows the greatest radiation stability, probably because of the anion's ability to scavenge precursors to the formation of H_2.

Resins exposed to environments with high relative humidity are capable of absorbing large amounts of water. Data presented in Table 1 show that at 100% relative humidity water contributes from 24% to 37% of the total mass of the samples depending on the anion in the resin. Thus, AmbCl and AmbOH retain 37% and 33% of water at about 100% relative humidity, whereas $AmbNO_3$ absorbs only about 24% of water under the same conditions. Obviously, the variation in water loading may also come from the differences in resin bead size. This variation must be considered when comparing water loading on AmbCl and $AmbNO_3$ to AmbOH, since these resins are purchased from different manufacturers. However, the comparison of water loading on AmbCl and $AmbNO_3$ remains fully justified, since the nitrate form has been prepared by the ion exchange from the chloride, and, therefore, inherited the same bead size distribution. The large difference in water loading between AmbCl and $AmbNO_3$ (37% vs. 24%) is due to the important role of the anion in water retention. Water is incorporated into porous resins and either binds to the anions with different efficiencies or the anions affect the number of water binding sites.

The contribution of water to the radiation decomposition of the various resins was first examined using humid samples from the environmental chambers. The radiation-chemical yield of H_2 is shown in Fig. 2 as a function of the water loading for Cl^- and OH^- forms of the resins. The presence of water increases the amount of H_2 produced and at the maximum water loading in a single phase system (water content of 24–37%) the yield of H_2 is more than double that of the dry samples. This increased H_2 formation, however, is still well below the $G(H_2) = 0.45$ molecules/100 eV found in pure water [23].

Table 1
Water loading (wt.%) as a function of relative humidity.

Relative humidity (%)	Water loading (%)		
	$AmbNO_3$	AmbOH	AmbCl
0	0	0	0
53	10.2	14.4	15.6
100	24.0	32.5	37.3

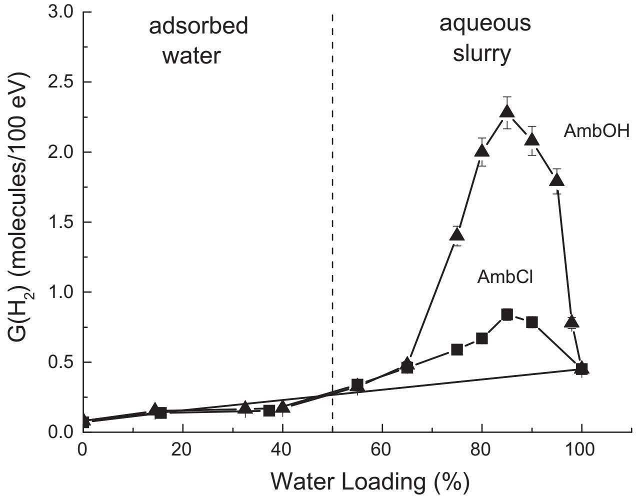


Fig. 2. Radiation-chemical yield of H_2 as a function of water loading on Amberlite™ resin in single phase systems due to adsorbed water and in aqueous slurries: (▲) OH^- form and (■) Cl^- form. The solid straight line shows the expected yield due to the mixture rule.

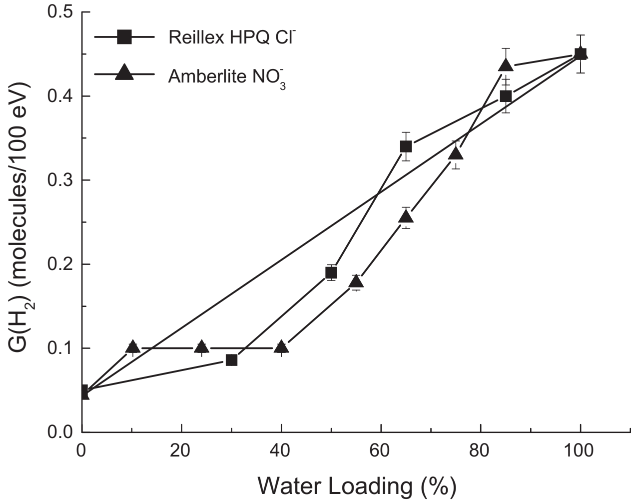


Fig. 3. Radiation-chemical yield of H_2 as a function of water loading for Amberlite™ nitrate (▲) and Reillex™ HPQ chloride (■). The solid straight line shows the expected yield due to the mixture rule.

The technique of loading water using humidity chambers could only achieve about 30% by weight of water. Larger amounts of water are usually encountered in realistic conditions and it is desirable to examine how H_2 formation in these systems approaches that for pure water. Slurries were prepared by the direct mixing of the dry resin and appropriate amounts of water to achieve the desired component resin/water ratio up to 100% water content. Fig. 2 illustrates the results for the yield of H_2 as a function of water loading in the radiolysis of AmbCl and AmbOH aqueous slurries. At the lower water content (up to about 50%) obtained in single phase systems, the H_2 formation basically follows the "mixture law", which states that the fraction of the total absorbed energy initially deposited to each component of the mixture is proportional to the mean mass collision stopping power (electron density or number of electrons per unit volume) of the component. Electron densities are proportional to the number of electrons per molecule divided by the molecular weight: 0.56 for water and 0.54 for AmbCl. Since the electron densities of the resin and water are very similar, the initial energy distribution in each component of the system is equivalent to the weight fraction of the component.

The results for H_2 production at water content greater than about 50% are surprising for AmbCl and AmbOH when considering the initial distribution of energy deposition and the "mixture law". A large amount of water in the system leads to the enhanced production of H_2 for AmbCl and AmbOH. This effect is especially well pronounced in the case of AmbOH radiolysis, where the yield of H_2 at the maximum of 85% water loading exceeds 2.2 molecules/100 eV. This value is about five times greater than the H_2 yield in pure water. The $G(H_2)$ in the radiolysis of AmbCl/water slurries also reaches a maximum at about 85% water with a value equal to 0.84 molecules/100 eV. In contrast, the H_2 formation in the radiolysis of $AmbNO_3$/water slurries is clearly suppressed as shown in Fig. 3; the deviation from the "mixture law" is on the negative side. A similar reduction in H_2 production is observed in the radiolysis of the Reillex™ HPQ chloride, a pyridine-based ion exchange resin (cf. Fig. 3). Radiolytic decomposition of resins representing the Reillex™ family has been studied in length before, however, H_2 formation studies at high water content was not performed in that work [11]. The pulse radiolysis study of pyridinium salts in aqueous solutions, which mimic the core functionality of Reillex™ resins, reveal that pyridinium systems rapidly scavenge solvated electrons as well as hydrogen atoms known to be precursors of H_2 [24]. These data provide a satisfactory explanation for the low H_2 production in Reillex™ HPQ chloride/water slurries.

Resin particle size may affect H_2 production by changing the amount of water absorbed or by variation of the surface area available for reaction. Amberlite™ resins in the dry state were ground into powder and then irradiated in the dry form and in slurries. There appears to be no difference in H_2 production between powdered and original sized samples irradiated in their dry state. However, at 75% water loading powdered $AmbNO_3$ exhibits a $G(H_2) = 0.26$ molecules/100 eV as compared to $G(H_2) = 0.33$ molecules/100 eV for original size beads. The yield of H_2 is increased by 0.1 molecules/100 eV for the powdered samples of AmbCl (75% water content) and decreased by 0.4 molecules/100 eV in AmbOH (75% water content) powder compared to the intact bead samples. All of the variations show no particular trend to lead to any reliable conclusions on the effects due to particle size or surface area. Different stirring and rotating techniques used during the radiolysis of two-phase resin/water slurries revealed that H_2 yield in these systems remained unaffected by mixing, which gives evidence that interfacial processes between resin and water do not play any significant role in H_2 formation.

3.2. Scavengers of e^-_{solv} and H_2 production

The formation of H_2 in neat water is mainly due to the reactions of the hydrated electron and its precursors [25–28]. The NO_3^- anion is a well known and widely used scavenger of hydrated electrons because of the high rate coefficient for this reaction (cf. Eq. (1)) [29]. In this work, no distinction will be made between the hydrated electron in bulk water and electrons associated with water absorbed in the resin. Both will be referred collectively as the solvated electron, e^-_{solv}, and the corresponding scavenging reaction of the NO_3^- anion is given as follows.

$$e^-_{solv} + NO_3^- \rightarrow NO_3^{2-} \qquad (1)$$

The results seem to suggest that the presence of nitrate anion is responsible for the low yield of H_2 in the radiolysis of $AmbNO_3$/H_2O mixtures (cf. Fig. 3). In comparison, the yields of H_2 with AmbCl and AmbOH are relatively higher than that found for $AmbNO_3$ because the hydroxide and chloride anions are poor scavengers of electrons (cf. Fig. 2) [29]. To further explore the effects of e^-_{solv}

scavenging, the H_2 yield from resin/water (25:75) slurries in the presence of NO_3^- anion at various concentrations was examined. Fig. 4 shows the results for the yields of H_2 as a function of nitrate concentration from slurries of each of the resins. All the resins demonstrate a similar and significant effect on H_2 production upon the addition of nitrate anion. An initial steep decrease of H_2 formation is followed by a more moderate decrease with increasing NO_3^-. An increase in NO_3^- concentration increases the probability of scavenging of the e^-_{solv} and thereby decreasing any product derived from its reactions. The radiolysis of AmbOH leads to the highest $G(H_2)$ compared to other resins at corresponding scavenger concentrations. Not surprisingly, $AmbNO_3$ demonstrates the lowest yield of H_2 compared to the other two resins even at very low concentrations of added NO_3^-. Apparently, NO_3^- ions present within the resin structure contribute to the overall quenching of molecular H_2 formation.

Two more conventional quenchers of e^-_{solv} were tested: nitrous oxide and oxygen since they also have high rate coefficients, but with very different products (Reactions (2) and (3)) [29]:

$$e^-_{solv} + O_2 \rightarrow O_2^- \tag{2}$$

$$e^-_{solv} + N_2O \rightarrow N_2 + O^- \tag{3}$$

The solutions were prepared by purging O_2 or N_2O, respectively, through the sample cell with slurry for 15 min. Both oxygen and nitrous oxide reduce the yield of H_2 to about half its value in the AmbCl/H_2O slurry (25:75) without any additives. These experiments clearly show the important role of e^-_{solv} in formation of H_2 from the resin/water slurries. However, the question remains whether e^-_{solv} is a direct precursor of H_2 or it is involved in processes giving rise to products that eventually decompose to produce H_2.

3.3. Heavy ion radiolysis

Transuranic waste materials decay by the emission of α-particles, which are known to have very different radiation chemical effects than γ-rays [30]. Accelerated beams of 5 MeV ^{4}He ions were used to simulate the α-particle radiolysis that Amberlite™ resins may experience in the nuclear industry applications. Because of the intratrack reactions of reactive intermediates, H_2 yields typically increase from γ-radiolysis to α-particle radiolysis. The yields of H_2 in the α-radiolysis were found to be 0.27, 0.41, and 0.19 molecules/100 eV for the dry Cl^-, OH^-, and NO_3^- forms of the resin, respectively. These yields are slightly higher than observed in γ-radiolysis with the NO_3^- form of the resin having the greatest radiation stability.

The ^{4}He ions radiolysis of the resin/water slurries generally gives the same trends as observed in γ-radiolysis, that is, enhanced H_2 formation is observed at high water loadings (>75%) for AmbCl and AmbOH. Experimental results for the yield of H_2 as a function of water loading with AmbCl are shown on Fig. 5 in comparison with the γ-ray results. As expected, the yield of H_2 is greater with ^{4}He ions than with γ-rays because of the increased importance of intratrack reactions.

The original cells used in the ^{4}He ion experiments had an imperfect design leading to separation of the two phases. Because the beam is horizontal and has a very limited penetration only the aqueous phase was irradiated in some situations. Further investigation lead to the discovery that H_2 production from the aqueous part of the slurry equaled or exceeded that from the corresponding resin/water mixture (cf. Fig. 5) even with complete stirring. The results suggest that significant H_2 was being formed due to the decomposition of organic compounds leached from the resin into water.

3.4. H_2 production in the radiolysis of water extracts from resins

Additional γ-radiolytic studies with aqueous extracts from resins were undertaken to further examine the extent of organics leached from the resin to the aqueous phase leading to the enhanced H_2 formation. H_2 measurements were made in the range of its maximum production (mixtures with high water content (>75%)). The most extensive studies were performed on the AmbOH slurries, whereas for AmbCl only two experimental points were taken (cf. Fig. 6). The results show that aqueous extracts alone from AmbCl and AmbOH exhibit equally enhanced (or even higher) H_2 formation as the corresponding resin/water slurries. In other words, the radiolysis of organic leached from the resin can be as important in the production of H_2 as the radiolysis of the resin itself.

3.5. Amine formation in radiolysis of quaternary ammonium compounds in water

The earliest reports on the radiation-induced degradation of polystyrene-based anion exchangers with quaternary ammonium

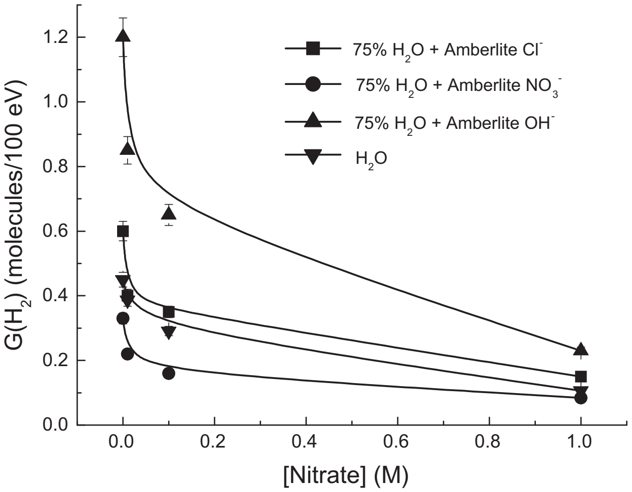


Fig. 4. Scavenging effect of nitrate on the radiation-chemical yield of H_2 from water (▼) and from resins in aqueous slurries (water content 75%): (■) Cl^- form, (●) NO_3^- form, and (▲) OH form.

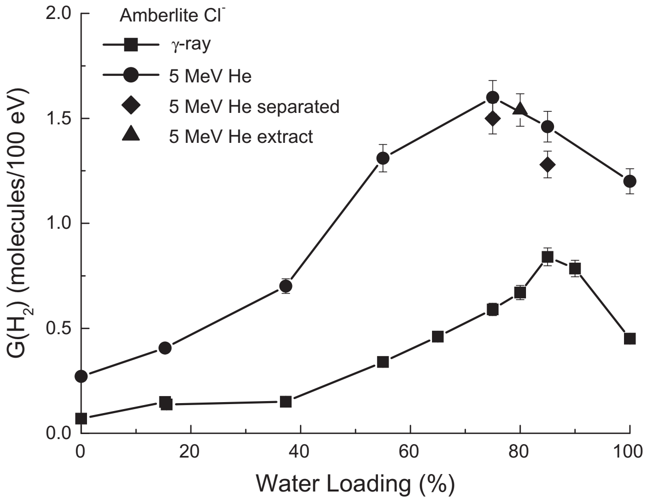


Fig. 5. Radiation-chemical yields of H_2 as a function of water loading on the Cl^- form: (■) γ-ray and (●) ^{4}He radiolysis of aqueous slurries; (◆) ^{4}He radiolysis of predominantly separated resin and liquid phase; (▲) ^{4}He radiolysis of water extracts from the resin.

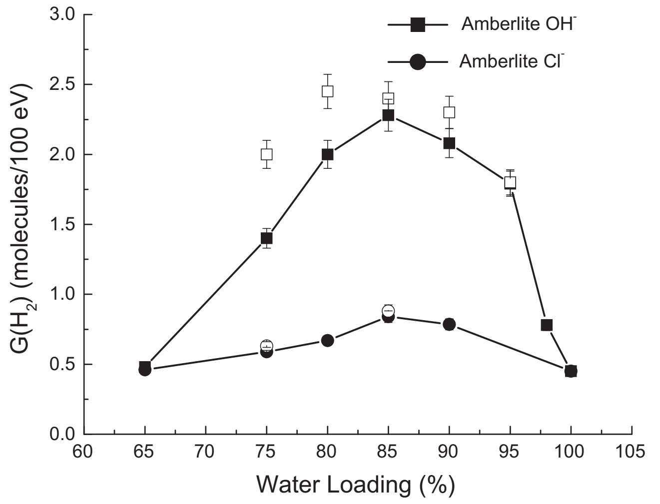
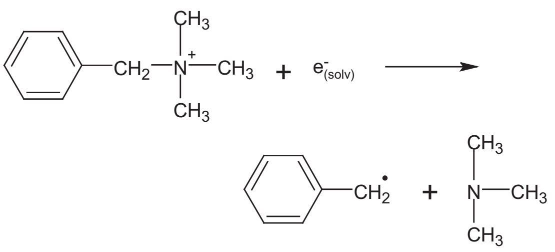


Fig. 6. Radiation-chemical yields of H_2 in the γ-radiolysis of aqueous slurries of the Cl^- form of Amberlite™ (●) and the corresponding extract from this resin (○) and in the γ-radiolysis of aqueous slurries of the OH^- form of Amberlite™ (■) and the corresponding aqueous extract from this resin (□).

functional groups appeared in the 50's of the past century [31,32]. These mainly qualitative studies focused on changes of resin's color, swelling and exchange capacity caused by ionizing radiation. Anion exchange resins with quaternary ammonium groups were found to exhibit rather poor radiation stability since they were shown to significantly lose their exchange capacity even at low doses. The decomposition of resins was accompanied by the formation of basic products [33]. The influence of the counter-ion on radiation stability of the resin was demonstrated by comparison of the radiolysis of the Cl^- and OH^- forms, and the Cl^- resin was shown to be more resistant than OH^- in the dose range up 350 kGy [34].

Hall et al. were the first to successfully identify and quantitatively describe the decomposition products from resins as tertiary, secondary and primary amines and ammonia [7]. In their work, trimethylamine was found to be a major product in the γ-radiolysis of Deacidite FF resin (in SO_4^{2-} and NO_3^- form). The yield of this tertiary amine exceeds 4 molecules/100 eV when the resin is irradiated in dry form, and $G((CH_3)_3N) = 3.2$ molecules/100 eV in aqueous slurries of the resin. This result is explained by the efficient deamination reaction taking place, which is caused by the direct effect of radiation on the resin and especially by the interaction of the quaternary ammonium group with e^-_{solv}, as shown by following reaction:



(4)

(4)

This type of reaction was investigated in detail in the γ-radiolysis of aqueous solutions of benzyltrialkylammonium cations $C_6H_5CH_2N^+(CH_3)_3$ [35,36]. The deamination reaction appears to be a very fast, diffusion-controlled process with a rate constant of $(4.3 \pm 0.2) \times 10^9\ M^{-1}\ s^{-1}$ [36]. Taking into account the abundant presence of e^-_{solv} in the radiolysis of water this reaction must play very important role in the deamination of Amberlite™ resins in aqueous slurries.

Hall and Streat suggested several alternative formation channels for dimethylamine, methylamine and ammonia also found in the radiolysis of Deacidite FF [7]. Dimethylamine can be produced by the decomposition of weak-base groups initially present in the structure of the resin or formed due to the decay of the original quaternary group (cf. Reaction (5)). This secondary amine may also be generated from the quaternary group directly (cf. Reactions (6) and (7), where R stands for the polymer matrix):

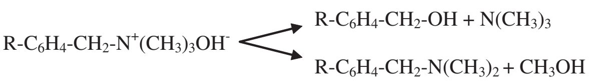
$$R{-}C_6H_4{-}CH_2{-}N(CH_3)_2 + H_2O \rightarrow R{-}C_6H_4{-}CH_2{-}OH + (CH_3)_2NH \tag{5}$$

$$R{-}C_6H_4{-}CH_2{-}N^+(CH_3)_3OH^- + H_2O \rightarrow R{-}C_6H_4{-}CH_2{=}N^+(CH_3)_2OH^- + CH_4 \tag{6}$$

$$R{-}C_6H_4{-}CH_2{=}N^+(CH_3)_2OH^- \rightarrow R{-}C_6H_4{-}CH_2OH + (CH_3)_2NH \tag{7}$$

A similar formation mechanism was proposed for methylamine and ammonia in that work. Also, further decomposition of $(CH_3)_3N$ and $(CH_3)_2NH$ released in the initial stages of radiolysis would eventually give simpler nitrogen-containing products, i.e. CH_3NH_2 and NH_3.

Along with the importance of the e^-_{solv}-driven deamination Reaction (4) heat-induced decomposition of quaternary ammonium hydroxides must be taken into account with respect to the trimethylamine formation. The Hofmann type degradation takes place in either of two ways [37]:



$$R\text{-}C_6H_4\text{-}CH_2\text{-}N^+(CH_3)_3OH^- \rightarrow R\text{-}C_6H_4\text{-}CH_2\text{-}OH + N(CH_3)_3 \tag{8}$$

$$R\text{-}C_6H_4\text{-}CH_2\text{-}N^+(CH_3)_3OH^- \rightarrow R\text{-}C_6H_4\text{-}CH_2\text{-}N(CH_3)_2 + CH_3OH \tag{9}$$

Studies performed with AmbOH reveal that the reaction channel generating $(CH_3)_3N$, Reaction (8), is slightly more favorable than Reaction (9) and corresponds to 60% of overall decomposition. Reactions (8) and (9) do not require extreme heat to become noticeable, for instance, it is recommended to keep the operation temperature below 60 °C when quaternary ammonium resins in the OH^- form are used [37]. Obviously, one may expect this decomposition to occur even in the lower temperature regime, only being less pronounced. Direct effects of radiation may also facilitate this degradation. Processes (8) and (9) must be definitely taken into consideration in our work when the radiolytic behavior of AmbOH is analyzed.

In Hall's and Streat's work spectrophotometric analysis was used for quantitative determination of trimethyl-, dimethyl-, and methyl-amines and ammonia following suitable derivatization [7]. Although all these analytic techniques seem to give reproducible and reliable results, the sample preparation is tedious and time-consuming. Modern analytic techniques offer better methods of observing amines in aqueous solutions by taking the advantage of the ability of amines to exist as ionic substances when they are transformed into salts. Thus, their quantitative analysis can be performed with high accuracy and sensitivity by means of ion chromatography.

Ion chromatography measurements revealed that several positively charged compounds are leached from the resins to the water, the major species are identified as trimethylamine and dimethylamine. Methylamine and ammonia were detected as well, but in much lower concentrations. Other minor peaks were observed in a few cases, which were caused either by impurities in the eluent

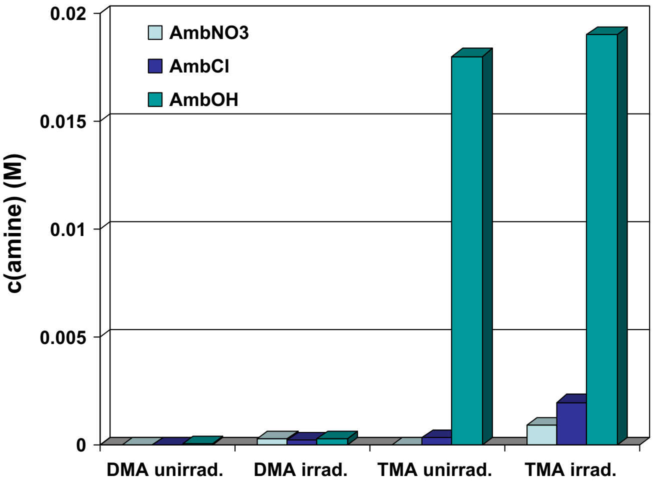


Fig. 7. Formation of dimethylamine and trimethylamine upon γ-irradiation of Amberlite™ in aqueous slurries (water content at 85%).

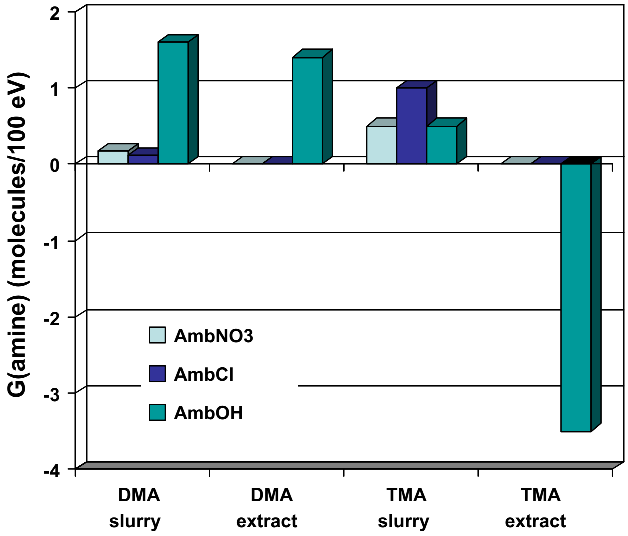


Fig. 8. Formation/decomposition of dimethylamine and trimethylamine upon γ-irradiation of Amberlite™ in aqueous water slurries (water content at 85%) and aqueous extracts from resins.

or were washed from resins. Their concentration did not show any dependence on the irradiation dose given and so they were ignored. Water extracts were taken both from the unirradiated water/resin mixtures and from the slurries exposed to irradiation. Fig. 7 and Table 2 give the results for H_2 yields with various anionic forms of Amberlite™. Dimethylamine is initially present at concentrations of tens of micromolar in all water extracts and a moderate irradiation dose of 16.6 kGy increases the concentration of this amine by about one order of magnitude. The result is observed for trimethylamine, with the exception that its initial concentration is relatively high even in unirradiated samples of Cl^- and OH^- resin forms (0.34 mM in water extract from AmbCl, 18 mM from AmbOH). The increase in trimethylamine concentration is relatively small (to 19 mM) when AmbOH/water slurry receives a dose of 16.6 kGy. The conclusion can be made that irradiation increases production of dimethylamine and trimethylamine in resin/water slurries. Nitrate anion seems to have a protective effect on the system, since the formation of trimethylamine is the lowest for $AmbNO_3$. This tendency can be better visualized by the presentation of yields of amines as shown in Fig. 8 and Table 3. *G*-values for the formation or decay of amines were determined both for the irradiated water/resin slurries and for the irradiated extracts. As can be seen in the figure, dimethylamine is formed with a higher yield if the resin is in contact in water compared to corresponding aqueous extracts. For AmbOH, the *G* (dimethylamine) in the slurry and in the extract are very similar and both are rather large. Interesting, $AmbNO_3$ along with AmbOH exhibit identical yields of trimethylamine (*G*(TMA) = 0.5 molecules/100 eV) when irradiated in slurries, whereas the AmbCl slurry produces twice that amount (*G*(TMA) = 1.0 molecules/100 eV). In contrast, the radiolysis of the aqueous extracts from $AmbNO_3$ and AmbCl are similar. The concentration of the trimethylamine does not change noticeably through the course of irradiation, that is, it remains dose-independent for these systems. In contrast, radiolysis of the extract from

Table 3
Formation/decomposition radiation-chemical yields (molecules/100 eV) of dimethylamine and trimethylamine upon γ-irradiation of Amberlite™ in aqueous slurries (water content at 85%) and aqueous extracts from resins.

Resin	Dimethylamine (DMA)		Trimethylamine (TMA)	
	Slurry	Extract	Slurry	Extract
$AmbNO_3$	0.17	0.003	0.5	0
AmbCl	0.12	0.003	1.0	0
AmbOH	>1.4	1.4	0.5	−3.5

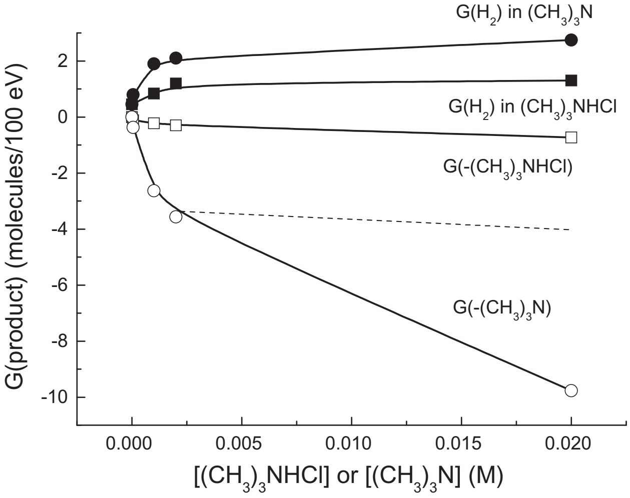


Fig. 9. H_2 yields in the radiolysis of aqueous solutions of (●) $(CH_3)_3NHCl$ and (■) $(CH_3)_3N$ and the loss of (○) $(CH_3)_3NHCl$ and (□) $(CH_3)_3N$ in their respective aqueous solutions. The loss of $(CH_3)_3N$ below the dashed line is probably due to evaporation.

Table 2
Formation of dimethylamine and trimethylamine (mol L^{-1}) upon γ-irradiation of Amberlite™ in aqueous slurries (water content at 85%).

Resin	Dimethylamine (DMA)		Trimethylamine (TMA)	
	Unirradiated	Irradiated (16.6 kGy)	Unirradiated	Irradiated (16.6 kGy)
$AmbNO_3$	1.0×10^{-5}	3.0×10^{-4}	3.0×10^{-5}	9.5×10^{-4}
AmbCl	1.0×10^{-5}	2.6×10^{-4}	3.4×10^{-4}	2.0×10^{-3}
AmbOH	6.1×10^{-5}	2.9×10^{-4}	1.8×10^{-2}	1.9×10^{-2}

Table 4
H_2 production yield (molecules/100 eV) and $(CH_3)_3N$ decay yield in the radiolysis of aqueous solutions of $(CH_3)_3NHCl$ and $(CH_3)_3N$.

$[(CH_3)_3N]$ (M)	$G(H_2)$ (molecules/100 eV) in $(CH_3)_3N$ solution	$G(H_2)$ (molecules/100 eV) in $(CH_3)_3NHCl$ solution	$-G((CH_3)_3N)$ (molecules/100 eV) in $(CH_3)_3N$ solution	$-G((CH_3)_3NHCl)$ (molecules/100 eV) in $(CH_3)_3NHCl$ solution
0	0.45	0.45	0	0
5×10^{-5}	0.8	–	0.4	0.12
1×10^{-3}	1.9	0.84	2.6	0.23
2×10^{-3}	2.1	1.2	3.6	0.3
2×10^{-2}	2.8	1.3	9.8	0.7

the AmbOH resin leads to a high decomposition yield of trimethylamine ($-G$(TMA) = 3.5 molecules/100 eV). Hence, when the concentration of trimethylamine is relatively high initially as in the case of AmbOH extract, it is consumed much faster compared to solutions with lower concentrations.

3.6. H_2 production in the radiolysis of methylamines and their hydrochlorides

Various types of methylamines are found to be present in the aqueous extracts from Amberlite™ resins with trimethylamine being the dominant one. From the literature, it is known that γ-radiolysis of gaseous CH_3NH_2, $(CH_3)_2NH$ and of $(CH_3)_3N$ at room temperature and atmospheric pressure produces molecular hydrogen in exceptionally high yields, typically exceeding 10 molecules/100 eV [38]. Despite the expected difference in the radiolytic decomposition pattern of gaseous amines and amines dissolved in water, the presented experimental findings strongly suggest that these basic compounds can significantly contribute to the total H_2 formation from aqueous solutions. To the best of our knowledge, only a few experimental studies addressed this issue [39,40]. The radiolysis of aqueous solutions of triethylamine was investigated by Clay and Rashid [39]. They find $G(H_2)$ in the radiolysis of 1 mM $(CH_3CH_2)_3N$ to be about 1 molecule/100 eV and it does not change significantly over a wide range of pH. Note that even at this low concentration of amine, the molecular hydrogen yield is roughly double that of $G(H_2)$ in pure water.

A series of radiation-chemistry studies have been initiated to determine the H_2 yield in radiolysis of trimethylamine in water. This exercise is intended to show whether aliphatic amines are responsible for the enhanced H_2 production from aqueous solutions. Obviously, the H_2 yield must be measured in the same concentration range of amine as found in the extracts from resins. There is a technical difficulty, however, involved in such experiments. $(CH_3)_3N$ is a volatile gas and it is quite a challenge to prepare its aqueous solutions with high accuracy directly. Therefore, the H_2 measurements were initially performed on the aqueous solutions of trimethylamine hydrochloride. Then, solutions of neutral amine $(CH_3)_3N$ were prepared by adding the appropriate amount of lithium hydroxide in equimolar concentration to $(CH_3)_3NHCl$ solutions. The results for the formation of H_2 as a function of concentration of the parent compound are shown on Fig. 9 and Table 4. The radiolytic decomposition of both $(CH_3)_3NHCl$ and $(CH_3)_3N$ in water leads to increased H_2 formation compared to pure water ($G(H_2) = 1.3$ molecules/100 eV in 0.02 M trimethylamine hydrochloride, $G(H_2) = 2.75$ molecules/100 eV in 0.02 M trimethylamine). In turn, the radiolytic decays of $(CH_3)_3NHCl$ and $(CH_3)_3N$ are concurrent with the H_2 generating processes.

Assuming that the major part of e^-_{solv} for Reaction (4) is supplied by the decomposition of water, it follows that in the radiolysis of AmbCl (or $AmbNO_3$) slurries one equivalent of e^-_{solv} is transformed into one equivalent of HCl and HNO_3, which eventually are neutralized by the released trimethylamine (Reactions (10) and (11)):

$$C_6H_5CH_2 - N^+(CH_3)_3Cl^- + e^-_{solv} \rightarrow C_6H_5CH_2\bullet + N(CH_3)_3 + Cl^- \quad (10)$$

$$H^+ + Cl^- + N(CH_3)_3 \rightarrow (CH_3)_3NHCl \quad (11)$$

On the other hand, trimethylamine is generated in neutral form in the radiolysis of AmbOH slurries (Reactions (12) and (13)):

$$C_6H_5CH_2{-}N^+(CH_3)_3OH^- + e^-_{solv} \rightarrow C_6H_5CH_2\bullet + N(CH_3)_3 + OH^- \quad (12)$$

$$H^+ + OH^- + N(CH_3)_3 \rightarrow (CH_3)_3N + H_2O \quad (13)$$

The results presented in Table 4 show that the radiolytic decomposition of neutral trimethylamine in water produces H_2 with yields double those from trimethylamine hydrochloride. This increased yield of H_2 matches well with the exceptionally high $G(H_2)$ in the radiolysis of AmbOH, where neutral $(CH_3)_3N$ is subject to decomposition. Radiolysis of AmbCl and $AmbNO_3$ give salts of trimethylamine that decompose with more moderate yields of $G(H_2)$.

The seemingly high decay yield of neutral $(CH_3)_3N$ at high concentrations is most likely caused by the increased volatility of the amine. The "imaginary" dashed line in Fig. 9 would represent more adequately the decay yield of $(CH_3)_3N$, although, unfortunately, experimental verification was not possible. The results give a strong indication of the important role of radiolytic decomposition of trimethylamine in the excess formation of H_2 upon irradiation of quaternary ammonium systems like Amberlite™ resins. This issue must be definitely borne in mind when quaternary ammonium containing anion exchangers are performing their tasks in scenarios with high ionizing radiation exposure.

3.7. Reflectance FT-IR spectroscopy of resin samples

An attempt was made to use Fourier transform spectroscopy in order to identify structural changes induced by γ-radiation in dry samples and in aqueous slurries. The IR spectra of all resins show almost no difference before and after radiolysis and for this reason are not shown here. The maximum dose achieved in our study was 0.3 MGy. Apparently this dose is too low to induce any noticeable changes in IR spectra. In a previous IR investigation of Zerolit FF-IP anion exchange resin, which is structurally similar to Amberlite™, doses up to 2500 MGy were applied to enable spectroscopic analysis of samples [41]. Obviously, the dose rate of 63.1 Gy/min used in this work would require prohibitively long times to reach such high dose. Nevertheless, even under the present experimental conditions the appearance of very subtle band at 2720 cm^{-1} was observed. Based on the literature, this band was assigned to the NH^+ group in trimethylamine hydrohalides [41]. This observation corroborates well the ion chromatography results, where formation of trimethylamine in the radiolysis of Amberlite™ resins is shown to be very efficient.

4. Conclusions

In this work yields of H_2 in the radiolysis of aqueous slurries of the quaternary ammonium anion exchange resin Amberlite™

IRA400 were measured. Three different anion forms of this resin (NO_3^2, Cl^- and OH^-) were examined. The anion is responsible for the difference in the sample water loading in environments of various relative humidity. In resins with high water content, the radiolysis of Cl^- and OH^- forms leads to enhanced H_2 production. Extended studies with various electron scavengers (NO_3^-, N_2O and O_2) prove an important role of e^-_{solv} in the formation of H_2 from these resins. Heavy ion (^4He) radiolysis of resin/water slurries follows the same trend as observed in γ-radiolysis: Cl^- and OH^- forms demonstrate an enhanced H_2 production at high water content. The increase in H_2 production in these systems was found to be due to compounds that leach from the resin to the aqueous phase. Ion chromatography studies have revealed that there are several compounds leached to the water, the major ones are identified as trimethylamine and dimethylamine. Yields of these amines in the radiolysis of aqueous slurries of resins were estimated. Strong experimental evidence for the radiolytic decomposition of amines, in particular trimethylamine, has been shown. Radiation-induced destruction of these amines leads to the excess H_2 production. The radiolysis of resin/water slurries also produces trimethylamine at high yields due to the effective deamination reaction taking place between e^-_{solv} and the quaternary ammonium group.

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