Chemistry

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1965

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Abstract

Full Text

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Absorption of Ammonia and Chlorine by Ion-Exchange Resins under Dynamic Conditions

Literature data on the interaction of ion exchangers with gases are almost absent. The only published study of such a process was carried out by E. Kreidar ([1]), who investigated under static conditions the absorption of ammonia by a strongly acidic cation exchanger in the H-form. In addition, there are patents for processes of purifying air from acidic and basic gases by means of moistened ion-exchange resins ([2],[3]).

In the present work we studied the sorption of ammonia and chlorine under dynamic conditions, respectively, by the cation exchanger KU-2 in the hydrogen form and by the anion exchanger AV-17 in the carbonate form.

Fig. 1. Dependence of the dynamic activity (A) of ion exchangers on their water content (W):
I –during absorption of ammonia by the cation exchanger KU-2 in the H-form;
II –during absorption of chlorine by the anion exchanger AV-17 in the CO_3-form.
Experimental conditions: ion-exchanger samples 25 g; ammonia concentration 4 mg/l, chlorine 150 mg/l; linear gas velocity 10 cm/sec; ion-exchanger bed length 12 cm; ion-exchanger particle size 0.5–1.0 mm; temperature 20°.

and by the anion exchanger AV-17 in the carbonate form. The method of preparing the ion exchangers was taken from the literature ([4]). The dried gases were passed through a thermostated dynamic tube into which the ion exchanger was placed. The dynamic activity of the absorbent—the ion exchanger—was determined as a function of the moisture content in the initial sample of ion exchanger, the granulometric composition, the height of the ion-exchanger bed, and the gas velocity and concentration. The conditions and results of the experiments are presented in Figs. 1–4. The dynamic activity is expressed as a percentage of the full static exchange capacity of the ion exchangers. The specific static capacity of the samples of ion exchangers tested was found to be 4.95 mg-eq/g (with

Fig. 2 and Fig. 3

Figure 2: Fig. 2 and Fig. 3

respect to NaOH) for KU-2, dried at 105°, and 3.82 mg-eq/g (with respect to HCl) for AV-17, dried at 60°. Breakthrough of gas through the ion-exchanger bed was recorded with a UG-1 gas analyzer. The sensitivity of determination was 0.004 mg/l NH_3 and 0.005 mg/l Cl_2.

The dependence of the dynamic activity (A) of the ion exchangers on their initial moisture content is most sharply expressed (Fig. 1). It should be noted that, before the onset of gas breakthrough, the water present in the ion exchangers did not contain appreciable quantities of dissolved gases; this was established by experiments in which ammonia and chlorine were passed through moist ion exchangers in nonreactive forms (the cation exchanger in the ammonium form, the anion exchanger in the chloride form). Gas breakthrough was observed practically immediately. Consequently, the solubility of the gases and their physical sorption, -

those considered apart from chemical interaction on the ion exchanger had no effect on the value of A. At the same time, the efficiency of gas absorption by ion exchangers decreases when their water content is below a certain minimum value. In the sorption of ammonia by the KU-2 cation exchanger in the H-form, the maximum A (98-99%) was reached, other conditions being optimal, if the ion exchanger contained not less than 20-23% water by weight. Reducing the moisture content of the ion exchanger to 10% leads to a decrease of A to 15%; with a further decrease in moisture content, the fall in dynamic activity slows, and an ion exchanger dried to constant weight at 105° still sorbs, before breakthrough, about 2% of the maximum amount of ammonia.

Fig. 2. Dependence of the dynamic activity (A) of ion exchangers on the gas concentration (C). Moisture content of the ion exchangers: KU-2 cation exchanger 30%, AV-17 anion exchanger 40%. The remaining experimental conditions and designations are the same as in Fig. 1

Fig. 3. Dependence of the dynamic activity (A) of ion exchangers on the length of the ion-exchanger layer (l). Moisture content of the ion exchangers as in Fig. 2; the remaining conditions and designations are the same as in Fig. 1

Although it cannot be ruled out that this residual activity of the dry resin is partly associated with traces of moisture retained by the ion exchanger at 105° (^{5}), it may be assumed that, alongside the ionic mechanism of the reaction in the presence of water,

$$(NH_3 + H_2O \rightarrow NH_4^+ + OH^- + RH \rightarrow RNH_4 + H_2O)$$

direct addition of ammonia to the sulfo groups of the ion exchanger also occurs ($RH + NH_3 \rightarrow RNH_4$). Approximately the same (about 3%) activity of

Figure 4

Figure 3: Figure 4

the dry resin is also observed in the sorption of chlorine by the AV-17 anion exchanger in the CO_3-form, which permits the assumption of a nonionic character of the interaction in this case as well. The low activity of dry ion exchangers in reactions with gases may be explained, first, by the inaccessibility of some of the functional groups of the ion exchanger in its unswollen state and, second, by the low probability of a sufficient approach of the gas molecule to the functional group of the ion exchanger—the event necessary for direct combination. If the latter factor is decisive for the kinetics of the reaction, then the activity of the dry ion exchanger should increase appreciably with a decrease in the gas velocity and an increase in the ion-exchanger layer, which can be clarified experimentally. Finally, the influence of physical sorption of the gas by the ion exchanger and of the thermodynamic conditions of the reaction must be determined. Of particular interest is the investigation of the reaction mechanism during the absorption of chlorine by an anion exchanger in the CO_3-form. Of the products of the interaction of chlorine with water ($Cl_2 + H_2O \rightarrow HCl + HOCl$), only hydrochloric acid can displace carbonic acid from the anion exchanger ($R'_2CO_3 + 2HCl \rightarrow 2RCl + H_2O + CO_2$), whereas hypochlorous acid ($K_a \approx 4 \cdot 10^{-8}$), weaker than carbonic acid ($K_{a_1} \approx 4 \cdot 10^{-7}$), should accumulate in the solution. However, in the aqueous phase of the ion exchanger only traces of hypochlorous acid are detected; the amount

the chloride ion displaced from the anion exchanger during desorption with a Na_2CO_3 solution corresponds to the entire amount of chlorine absorbed.

Thus, hypochlorous acid either undergoes oxygen decomposition ($2HOCl \rightarrow 2HCl + O_2$), or oxidizes negatively charged nitrogen with the formation of chloramine. The latter reaction may proceed intensively at intermediate pH values in the presence of ammonia compounds [6], represented in this case by the functional groups and impurities of the anion exchanger. It was noted that after absorption of chlorine the anion exchanger becomes decolorized, but restores its original light-brown color during alkaline desorption. The capacity and dynamic activity of the ion exchanger were fully restored during desorption. Apparently, the oxidizing action of chlorine and hypochlorous acid was expressed in the reversible oxidation of impurities in the ion exchanger and did not affect the functional groups of the ion exchanger.

Fig. 4. Dependence of the dynamic activity (A) of ion exchangers on the linear (V_l) and volumetric (V_0) gas velocity. Moisture content of the ion exchangers as in Fig. 2; other conditions and designations are the same as in Fig. 1.

An exothermic effect was observed for the reactions of interaction of the cation exchanger with ammonia and of the anion exchanger with chlorine, increasing with increasing gas concentration. Evaporation of water, which occurs when the temperature rises in the gas-absorption zone, possibly explains a certain decrease in the dynamic activity of the ion exchangers as the gas concentration increases (Fig. 2). The maximum dynamic activity was reached at an ion-exchanger bed height of 12-15 cm (Fig. 3). Increasing the gas velocity within the investigated range of its values slightly lowered the dynamic activity (Fig. 4), which may be connected with kinetic factors.

The influence of the granulometric composition of the ion exchanger was investigated during sorption of ammonia by the KU-2 cation exchanger. It was found that, for an ion exchanger newly put into operation, with grain sizes from 0.2 to 1.0 mm the dynamic activity remains constant, while for the fractions 1.0-1.2 and 1.2-1.5 mm it decreases by 3-4 and 8-10%, respectively. The dynamic activity of an ion exchanger that had undergone 5 sorption-desorption cycles did not change relative to the initial value for the 0.2-0.5 mm fraction, but already for the 0.5-0.75 mm fraction a decrease in A by 3% was noted, for the 0.75-1.0 mm fraction by 10%, and for the 1.0-1.5 mm fraction by 20%.

The investigation carried out, which is only one of the first steps in the study of gas-absorption processes by ion-exchange substances, shows the great promise of this direction in both applied and theoretical aspects, since any chemically active gases and vapors can be absorbed on ion exchangers.

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Received
5 IX 1964

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