

GAS HOLDUP IN BUBBLED BEDS OF AQUEOUS SOLUTIONS OF ELECTROLYTES

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Gas holdup in dependence on velocity is studied experimentally at bubbling of aqueous solutions of electrolytes. In all, 22 various types of electrolytes were measured and the obtained data were correlated according to the existing relations. It results that the gas porosity differs considerably with individual types of electrolytes and that their absolute values cannot be reliably estimated for the time being without at least one experimental pair of values porosity-velocity. Approximate procedures for estimates of this quantity are proposed.

A relation for the mean relative gas holdup (porosity) in the bubbled bed of liquid (IS system of units) has been recently¹ derived in the form

$$e = \frac{1}{2^{4/5}} \frac{1}{4^{1/5}} (1/g)^{4/15} (\rho_G/\rho_L)^{4/15} D^{4/15} (\mu_G/\rho_G)^{1/5} K^{7/15} \cdot v^{4/5} / (2v + 0.2)^{7/15}, \quad (1)$$

which with a good accuracy correlated the experimental dependences $e-v$, where v was the linear gas velocity. The relation (1) includes two empirical parameters D and K . We assume for any gas-liquid system a constant value of parameter D ($D = 1.74 \cdot 10^3$ determined experimentally for the water-air system) while the parameter K is variable and is characteristic for the given bubbled gas-liquid system. For solution of non-electrolytes, the value of K can be determined¹ if the interfacial tension and liquid viscosities are known. A similar dependence of parameter K on physico-chemical parameters of the system for aqueous solutions of electrolytes has not been found¹. Thus we have studied a wide series of various types of solutions of electrolytes in water with an aim to describe the specific behaviour of individual electrolytes from the point of view of gas holdups at bubbling. The results are presented in this study.

EXPERIMENTAL

Column. Porosity measurements were performed in a column 150 mm ID, with a distributor formed by a plate with circular holes with $d = 1.6$ and $\phi = 0.03$. Plates with other geometrical characteristics have not been investigated since we have proved earlier a negligible effect of plate

geometry on the character of the bubbled bed. The height of the bubbled bed is 1200 mm at max. The gas chamber below the distributor was equipped by another perforated plate with $\varphi = 0.005$ situated 100 mm below the distributing plate.

Measurement of mean porosity. Mean porosity was determined manometrically by measurement of the static liquid pressure along the bed height. Porosity in the section between two manometric taps situated at x_{i+1} and x_i is given by the relation $e_{i+1,i} = (y_{i+1} - y_i)/(x_{i+1} - x_i)$. The heights of liquids y in manometers are measured from a common origin which is in the plane of the distributing plate. As the porosity varies along the bed height (it increases) the mean porosity must be calculated as an integral along the whole bed height. It has been found that the mean porosity, which is practically identical with the integral value, can be obtained much easier as the slope of the straight line of a section in the dependence $\Delta y_{i+1} - x_i$, which corresponds to constant values of porosity in the central portion of the bubbled bed *i.e.* without boundary regions in vicinity of the plate and at the upper surface of the bubbled bed. The changes in porosity along the bed height, with the constant value in the central portion of the bed have been discussed earlier. Through experimental points of static pressures in the central part of the column was plotted an optimum straight line by the least square method. So found porosity was considered to be the mean porosity e . Distance of the neighbouring manometer taps in the column wall was always 50 mm.

Solutions of electrolytes. In all 22 aqueous solution (mostly 1M) of the following inorganic compounds were measured: $K_3Fe(CN)_6$, $K_4Fe(CN)_6$, $FeCl_3$, $Al(NO_3)_3$, NaF , $NaNO_3$, KCl , $NaCl$, NH_4Cl , $NaClO_4$, $NaSCN$, Na_2CrO_4 , Na_2CO_3 , $COCl_2$, Na_2SO_3 , Na_2SO_4 , $MgCl_2$, $CdCl_2$, $CaCl_2$, $BaCl_2$, $NaHPO_4$, $CuSO_4$. These compounds were selected so that various combinations of anions and cations were represented with variable sizes of ions. The range of basical physico-chemical characteristics of studied solutions of electrolytes is so wide that on basis of the obtained results qualitative conclusions concerning the studied system could be made.

Measurement. During measurement of porosity of electrolytes the hysteresis on curves of dependences $e-v$ was determined according to the path by which the system was brought into the steady state at which the measurement took place. Results of mean porosities at the given superficial gas velocity presented here are valid for the regime fixed at the decreasing gas flow rate.

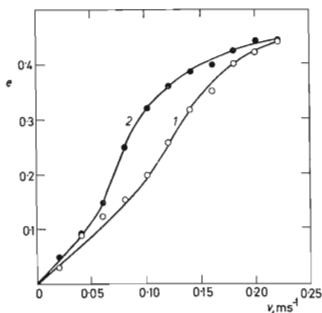


FIG. 1

Hysteresis of Porosity According to the Path by which the State Was Reached

1 ↑ Increasing gas velocity, 2 ↓ decreasing gas velocity.

The differences in porosities ascribed to the hysteresis were different with all the measured solutions of electrolytes. An example of a hysteresis is plotted in Fig. 1. The liquid flow rate which affects considerably the measured porosity was in all our measurements equal to zero.

Correlation of experimental porosities. Experimental porosities were correlated: 1) According to the relation we have derived earlier (1) and by the relations mostly cited in literature: 2) According to Reith²

$$e = v/(2v + k_1) \quad (2)$$

derived on a model based on the character of motion of bubbles in the bubbled column where k_1 is for solutions of electrolytes given as a universal constant equal $k_1 = 18 \text{ cm s}^{-1}$; 3) According to Akita and Yoshida³ which in an arranged form equals

$$e/(1 - e)^4 \approx k_2 v. \quad (3)$$

The relation (3) was derived as a general empirical relation for solutions both of nonelectrolytes and electrolytes by the dimensional analysis. The coefficient k_2 is a function of physico-chemical macroparameters of the system only, for the electrolytes is proposed a corrected constant for the right hand side of Eq. (3). The optimum values of K , k_1 and k_2 in relations (1) to (3) were calculated for individual solutions of electrolytes by the least square method from our experimentally determined dependences $e-v$. Further the model⁴ dependence $e-v$ according to Eq. (2) and (3) was calculated with the values of k_1 and k_2 recommended by the authors.

RESULTS AND DISCUSSION

We have demonstrated experimentally that porosities, at otherwise identical conditions, differ considerably for individual solutions of electrolytes while absolute differences in porosities can be more than twice greater (constants $K = 680$ to 2960) while the porosity of some of solutions of electrolytes can be smaller than for the water bubbled by gas. It has been concluded that in the region of superficial gas velocities from 0 to 0.03 m s^{-1} the dependence $e-v$ (in the range of experimental accuracy of determination of porosities by the used method) can be best expressed by straight lines with different slopes for individual systems. This conclusions is in agreement with the experiments performed earlier⁵. But all systems deviate considerably from the linear dependence above the quoted linear gas velocity.

In the relations published for porosities of bubbled beds (our relation (1) inclusive) only one continuous dependence $e-v$ is assumed in the whole region of practically suitable superficial gas velocities for the bubbled bed *i.e.* from 0 to 0.3 m s^{-1} . Thus it is necessary to expect that by the use of one correlation relation for expressing porosities of the bubbled bed in the whole region of linear gas velocities, the porosities calculated in the region of low linear gas velocities v will be affected by an error.*

* It must be noted that in the region of small gas velocities and thus of low porosities as well, the experimental determination of the relative gas content is inaccurate and is affected by a considerable error.

Our relation (1) is expressing at best the experimentally determined trend of dependence $e-v$ of all the compared relations (1) to (3). The optimum constants K are given in Table I. Also the optimum values of constants k_1 and k_2 for individual solutions of electrolytes were determined⁴ which differed considerably for individual cases of the measured serie of electrolytes (*e.g.* the constant k_1 is varying for the measured set of solutions from 5 to 50 as expected). The plot of experimental data with the correlation for 1M-KCl is demonstrated in Fig. 2. Relations (2) and (3)

TABLE I
Constant K from Eq. (1) for Solutions of Electrolytes

Aq. solution of electrolyte 1M	Ionic strength	K	Deviation, % for $v = 6$ cm s ⁻¹	ρ_L g cm ⁻³	μ cP	e^a $v = 0.1$ ms ⁻¹	Standard rate of foam collapse
K ₃ Fe(CN) ₆	6	2 958	38	1.162	1.191	0.336	20.1
K ₄ Fe(CN) ₆	5	2 726	38	1.071	1.0315	0.322	31.8
FeCl ₃	6	1 835	18	1.144	1.7223	0.226	6.4
Al(NO ₃) ₂	6	834	13	1.159	1.9143	0.177	2.0
NaF	1	2 219	37	1.036	1.093	0.263	13.0,
NaNO ₃	1	2 001	26	1.049	0.9614	0.253	—
KCl	1	1 587	20	1.047	0.9153	0.224	9.1
NaCl	1	1 498	26	1.034	0.9831	0.215	8.3
NH ₄ Cl	1	1 065	16	1.016	0.908	0.197	9.8
NaClO ₄	1	821	10	1.074	0.940	0.165	4.0
NaSCN	1	620	17	1.039	—	0.142	10.8
Na ₂ CrO ₄	3	2 106	6	1.117	1.3015	0.268	10.4
Na ₂ CO ₃	3	1 681	16	1.103	1.5389	0.220	8.3 ^b
COCl ₂	3	1 620	17	1.116	1.3192	0.225	10.9
Na ₂ SO ₃	3	1 462	11	1.081	1.2309	0.222	13.0
MgCl ₂	3	1 338	11	1.072	1.3069	0.222	5.9
Na ₂ SO ₄	3	1 276	18	1.121	1.4085	0.212	16.3
CdCl ₂	3	1 087	18	1.157	1.1842	0.210	8.8
CaCl ₂	3	1 065	9	1.079	1.172	0.198	7.7
BaCl ₂	3	684	8	1.170	1.139	0.166	6.4
NaHPO ₄ (0.25M)	3/4	1 627	15	1.032	1.0423	0.245	—
CuSO ₄ (0.5M)	2	847	8	1.076	1.2028	0.168	—
H ₂ O	—	797	5	1	1	0.175	1.9

^a Porosity at $v = 0.1$ m/s, ^b time of foam collapse to 1 cm height.

with a universal value of constant k_1 and k_2 proposed by the authors are not quite suitable for calculation of porosities of electrolytes. With relation (3) is that because the densities, viscosities and surface tensions of aqueous solutions of electrolytes do not differ considerably and, consequently, the calculated plot $e-v$ will not generally differ much from the plot given in Fig. 2 for the solution of KCl. But at the same time we know that the experimental dependences $e-v$ do differ significantly according to the kind of compound. Mean deviations of the model and experimental porosities are also given in Table I. The correlation proposed by us (1) is reliably suitable for solutions of electrolytes for gas velocities $v = 6$ cm/s. The calculated porosities for velocities in the region $2 \leq v \leq 6$ could differ (by 30% at max. at small gas velocities below $v = 2$ cm/s the correlation is a very rough approximation. The mean deviations given in Table I are affected by inclusion of porosities for $v = 2$ cm/s which porosity is affected by a considerable error. The disagreement of the correlation (1) for small gas velocities is obviously due to very simplified model assumptions made at the derivation of relation (1) concerning the behaviour of the heterogeneous bed. The deviations in porosities are most profound just at small gas velocities v , when the absolute porosities are small.

In spite of that the proposed correlation (1) fits at best the actual porosities of solutions of electrolytes in the whole measured range of gas velocities from 0 to 35 cm/s in comparison with the other proposed relations, the behaviour of some groups of electrolytes that we have studied cannot be expressed satisfactorily as demonstrated also by the magnitude of relative deviations which are given in Table I. The explanation should be sought obviously in the formation of quite specific structures of various types of electrolytes at bubbling which are dependent on a whole number of various factors such as impurities, surface active compounds *etc.* All parameters af-

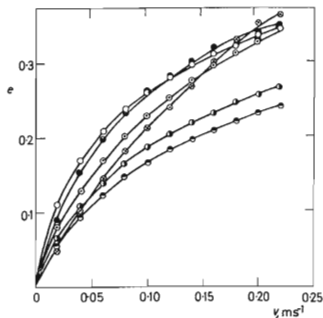


FIG. 2

Porosity of 1M Solution of KCl in Dependence on Velocity

⊙ Experimental data, ○ relation according to Akita and Yoshida³, $k_2 = 8.867$ calc. from experimental data and Eq. (3), ⊕ Akita-Yoshida³, $k_2 = 3.467$ calc. according to the correlation³ for non-electrolytes, ⊙ $k_2 = 4.337$ calc. according to the published correl.³ for electrolytes, ⊖ rel. (1), $K = 1.542$ calc. from experimental data, ● correlation according to Reith², $k_1 = 18$ cm. s⁻¹.

fecting the structure of the bed have not yet been described and in this respect nor were we successful. It cannot be even assumed that such a complex parameter as is porosity could be expressed fully by a simple relation (1) which was derived at very simplified assumptions of an existing analogy between the gas flow through a bubbled bed and through an equivalent pipe¹.

Though we have studied behaviour of a quite wide number of solutions of electrolytes, the negative conclusion drawn earlier is confirmed that it is not possible to correlate porosities (*i.e.* the constant K) of solutions of electrolytes by use of standard physico-chemical properties such as density, viscosity, and surface tension (the latter being measured by the method of separation of Pt ring). The experimental surface tensions are for all studied solutions statistically identical, in the range of the accuracy of the method. We have made an attempt to find a dependence of K on the ionic strength and the data published on the density of surface potential. The last parameter has been published for some of solutions of electrolytes in literature⁶, but the experimental determination has been performed⁶ for solutions of very pure salts which was not our case; in our study analytical and technical grade reagents were used. The conditions of an absolute purity of used compounds will not be met either with the industrial compounds which are of prime technical interest. The only indication pointing to some possible effect of surface potential on porosity and thus on the value of K , was the extremely small experimental porosity of the solution of 1M-NaSCN, *i.e.* of the salt which according to literature has extreme surface potentials from all the measured and quoted electrolytes. The effect of ionic strength is not unique.

We have also made an attempt to find a relation between the porosity and some other easily measurable property of an actual solution of electrolytes which could

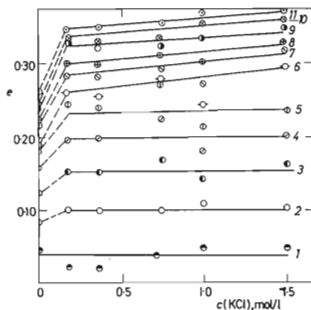


FIG. 3

Mean porosity in Dependence on Concentration of Solution of Electrolytes

1 $v = 0.02$ m/s, 2 0.04, 3 0.06, 4 0.08, 5 0.10, 6 0.12, 7 0.14, 8 0.16, 9 0.18, 10 0.20, 11 0.22.

characterize the global effect of all so-far unknown physico-chemical (electrochemical) parameters on the character of the formed bubbled bed. Such a characteristic property of bubbled beds was considered to be the rate of collapse of a foam formed by a pool of liquid bubbled in a standard way. The electrolytes used are forming in all cases so-called reversible foams, *i.e.* such structures which spontaneously get down in several seconds after stopping the bubbling. Procedure in the experiment: By a valve a gas velocity $v = 0.22 \text{ ms}^{-1}$ has been set in the column 0.085 m ID with the distributor formed by a perforated plate $\varphi = 0.005$. The liquid holdup was 1500 ml of measured solution and the measurement has been performed at constant temperature 25°C . After 3 min of keeping at constant gas flow rate the gas was stopped and the time was determined in which the foam collapsed. The measurement was stopped when the foam collapsed so that a clear-liquid surface was observed in the centre of the column. Each experiment was repeated several times and the agreement was surprisingly good. The results are given in Table I.

Though it is not possible to state quite clearly that there is a relation between the time of foam collapse and the porosity (constant K), certain trends can be observed. The constant K is directly proportional to the time of collapse for electrolytes with ionic strength $I = 1$ and $I = 6$. The exception make solutions of NaSCN and NH_4Cl . The group of electrolytes with the ionic strength equal to 3 did not have any relation to the rate of foam collapse. It can be said that solutions of electrolytes having the cations and anions in the combination of valencies 1-1, -1-3 or 3-1 behave so that there is a dependence of the constant K on the degassing rate. Without any relation to this behaviour are combinations of valencies with two cations or anions *e.g.* combination 1-2. This means that this method can be used in some cases for an estimate of the constant K but the method is not quite safe.

As concerns the shape of dependence of porosities on the gas velocity represented by the correlation (1), the following tendencies can be observed:

Positive behaviour: The actual curve $e-v$ gives in the region for velocities smaller than $v = 0.12 \text{ ms}^{-1}$ greater experimental porosities than those calculated (FeCl_3 , Na_2HPO_4 , CdCl_2 , $\text{Al}(\text{NO}_3)_3$).

Negative behaviour: Experimental porosities are in the region for velocities smaller than $v = 0.12 \text{ ms}^{-1}$ smaller than those calculated and above the given velocity they are greater (NH_4Cl , KCl , NaCl , NaSCN).

Neutral: Theoretical curve represents well the experimental data in the whole region of gas velocities (Na_2SO_4 , Na_2CrO_4 , CaCl_2 , CuSO_4 , H_2O , BaCl_2 , CoCl_2 , Na_2SO_3 , MgCl_2 , NaClO_4). Completely atypical (S-shape) is the shape of curves for $\text{Fe}(\text{CN})_6^{3-}$ and of $\text{Fe}(\text{CN})_6^{4-}$.

Finally, it can be said that the absolute porosities and the dependence of porosities on the gas velocity are so individual for various electrolytes that their expression by a single correlation relation with one constant is – with the exception of salts

where the constant K is known — practically impossible. The proposed relation in this case is a relatively good approximation if we know at least one pair of data $e-v$ and the constant K can be calculated for the relation (1). An estimate of the dependence $e-v$ can be than made for the whole range of v surprisingly well. In the region of velocities $v = 0-3 \text{ cm s}^{-1}$ the dependence of porosities is reasonably linear, *i.e.*

$$e = K'v \quad (4)$$

and the constant K' can be determined for individual solutions of electrolytes experimentally.

As we are usually interested in determination of porosity of solutions of electrolytes in relation to mass transfer with a chemical reaction *i.e.* for cases in which the solution is a complex systems of ions, it is usually impossible to use K values determined for simple solutions, moreover, from compounds selected from another point of view than those given in Table I. For solutions of carbonates and sulphites of alkali metals which come into account for use in model reactions for determination of mass transfer the mean value of $K = 1500$. This value can be used as a very rough approximation for an estimate of the effect of the type of electrolyte on porosity by its substitution into the relation (1). But so arranged relation is then practically of the same standard as the earlier criticized relations (2) and (3) except that the shape $e-v$ will be more reliable by this approximation. We would like to stress that with regard to other inaccuracies in determination of other parameters of the bubbled bed in reacting systems, the accuracy of the proposed estimate of porosity is usually quite sufficient.

Dependence of mean porosity on concentration of electrolytes. The present results and discussion concerned 1M solutions of electrolytes. In Fig. 3 is demonstrated that the concentration represents a value in the region $0.2 < M < 4$ when the porosity of the bubbled bed is practically independent of concentration. This figure also demonstrates an interesting dependence of porosities in the region of small concentrations where not only the dependence on concentration of the electrolyte is obvious but where the dependence of porosity can also change with the linear gas velocity. The dependence of concentration is practically identical for other solutions.

In the region of conc. $0-0.2M$ the linear interpolation for $0.2M$ solution and water can be made.

LIST OF SYMBOLS

- c concentration
- d diameter of holes of the plate
- D universal constant
- e mean porosity of the bed

- g gravitational acceleration
 K constant of electrolyte
 k_1 universal constant
 v superficial gas velocity
 x position of the manometer tap
 y height of liquid column in the manometer tube
 φ free plate area
 μ viscosity
 ρ density

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