

Studies on debromination of sea water and aqueous sodium bromide bromate solution

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Model proposed by Wagner *et al.* for distillation data considering gas phase resistance as the controlling resistance is modified in the present study wherein instead of gas phase resistance liquid phase resistance is considered as the controlling resistance for mass-transfer. This has been successfully applied to the experimental data collected during process development for recovery of bromine from brine employing air-blowing method. Experimental data collected are evaluated based on the modified model of Onda *et al.* and Wagner *et al.* Calculated values of mass transfer coefficients tally well with the observed values of mass transfer coefficient. Packed column performance is also compared with the results of Castillo *et al.* for removal of volatile organic compounds by steam stripping from water, wherein values of volumetric liquid phase mass transfer coefficient ranged from 0.001-0.008 (1/s) whereas in the present study it ranges from 0.0006-0.0164 (1/s).

Keywords: Bromine, Sodium bromide-bromate solution, Air blowing process, Liquid phase mass transfer coefficient, Interfacial area, Randomly packed column, Volatile organic compounds

Packed columns have been used extensively for distillation, absorption, stripping and extraction in chemical process industry. Columns are usually filled with randomly arranged dry packings of ring or saddle type. In literature, most of the experimental investigations on mass transfer rates with air-water system have been reported on random packings. While there is increasing interest in the regular packings (mesh, grids etc.), their applications tend to be limited by cost factor and incomplete performance documentation. Hydrodynamic and mass-transfer models, empirical or semi-theoretical for packed columns, have been published in the literature¹.

For random packings, the method of Cornell *et al.*² utilizes the two-film model and empirical parameters specific to each packing type and size. Onda *et al.*^{3,4} developed a random packing model based on a modest size data set, using the two-film model based on ceramic rings and saddles packings. Bolles and Fair⁵ expanded the Cornell *et al.*² data base and adapted the model to new experimental results taken at larger scales of operation. They included distillation results for Pall Ring random packings in their analysis. Bravo and Fair⁶ used the Onda model^{3,4} plus the Bolles-Fair⁵ data base to provide a correlation for effective interfacial area in randomly packed columns.

Knowledge of fluid dynamic behaviour is quintessential for column design and the prediction of mass transfer. The pressure drop studies of Stichlmair *et al.*⁷ compared the behavior of packed columns with the experimental findings for a fluidized bed which resulted in slight modification of the Ergun model for fixed bed of packing. Determination of the irrigated pressure drop across the packed column takes into account the rise in interstitial gas velocity with diminished flow area due to the presence of the flowing liquid. The model of Stichlmair *et al.*⁷ for irrigated pressure drop is considered by many investigators as the most fundamental model available which includes the determination of liquid hold-up both below and above the loading point.

The liquid hold-up in a packed column is defined as the volume of liquid held under operating conditions per volume of packed bed, which can be divided into static and dynamic hold-up. The static hold-up consists of the liquid kept in the voids or dead spaces of the packing, while the dynamic portion flows down the column. The static hold-up is influenced by the physical properties of the liquid and the packing surface but it is independent of the liquid load. The dynamic holdup is a function of the liquid velocity and is independent of gas velocity for various liquid loads below the loading point. In the loading

zone, however, the holdup increases as gas velocity approaches the flooding point. The holdup relationship given by Stichlmair *et al.*⁷ has been validated for air-water system upto liquid viscosity 5 centi poise. The equation used by Stichlmair *et al.* for liquid holdup is similar to that of Billet and Mackowiak⁸, but does not include a constant that depends on the packing type. Billet⁹ has given correlation between Froude number and liquid holdup based on the data for eight different packings under and above the loading point. Rocha *et al.*^{10,11} and Gaulito *et al.*¹² suggested that the liquid holdup is the parameter that links mass-transfer and momentum balances. Extension of the Stichlmair *et al.*⁷ treatment for liquid holdup, irrigated and flooding pressure drop predictions is given by Engel *et al.*¹³ for both structured and random packings. Castillo *et al.*¹⁴ considered hydraulic operation and mass-transfer process simultaneously by using the Engel *et al.* model for the design and analysis of packed columns for steam stripping of volatile organic compounds from water.

The effective gas-liquid interfacial area in randomly packed distillation or absorption column is basic parameter that affects the mass transfer. Various methods are available in the literature for prediction of the effective interfacial area during absorption with and without chemical reaction. But there exists a considerable amount of discrepancy regarding the values of the effective interfacial area. The correlations developed by various investigators are not comparable under otherwise similar conditions. It has been observed that the interfacial area is smaller than the total gas-liquid surface area. This is caused by negligible liquid flow through thin liquid films making the wetted surface largely ineffective for mass transfer. A part of the gas flow cannot interact with the liquid because of maldistribution of gas caused by liquid-filled voids which block the gas flow. Bornhutter and Mersmann¹⁵ and Fair and Bravo¹⁶ proposed that a large part of the effective interfacial area results from liquid drops generated in the packed column. Bornhutter observed that the contribution of drop flow ranges from 5-45% of the total liquid flow depending on packing type and liquid properties. Bravo and Fair⁷ have reported that the amount of effective interfacial area in a given system is the same for gas and liquid side mass transfer. Relationship between effective interfacial area and actual packing surface has been developed by several

researchers^{3,4,17-24} with the help of dimensionless Reynolds, Froude, Capillary and Weber numbers. Castillo *et al.*¹⁴ adjusted the fraction of wetted to packed area by following statistical analysis. Shi and Mersmann²⁴ took into account the wettability of the packing surface for metallic, ceramic and plastic packings.

In absorption and desorption application involving sparingly soluble solute, liquid side mass transfer resistance is generally dominant. It is evident from the above cited literature that the only consistence factor in the correlations for liquid side mass-transfer coefficient is 0.5 exponent of the diffusion coefficient as predicted by the penetration model of Higbie²⁵, whereas for gas side mass-transfer coefficient, the diffusion coefficient is having 0.66 power instead of 0.5. This might be owing to non-prediction of gas side mass-transfer by the penetration model.

Bromine, one of the halogen group elements non-metallic liquid, is manufactured by air-blowing and steaming-out process from seawater, brines and bittern (end liquor left after salt production from seawater)²⁶. Major steps involved in the process are:

- Oxidation of bromide to bromine, at pH 3-3.5 using chlorine gas.
- Removal of liberated bromine from the liquor either using steam or air.
- Condensation of steam-bromine mixture in case of steaming out process or fixation of bromine from the mixture of air-bromine as bromide salts in the presence of suitable alkali or sulfur dioxide.
- Liberation of bromine from alkaline mixture by acidification or chlorination in case of sulfur dioxide and steaming out the free bromine as in steaming-out process.
- Purification of crude bromine.

Systems involved in recovery of bromine are bromine-sea water, brine, bittern etc. which vary in chemical composition and some time saturated with respect to dissolved salt. In the present paper an attempt is made to analyze the performance of the packed column using models developed by various investigators with the help of experimental data collected during process developmental study (air blowing) for recovery of elemental bromine from sea water and aqueous sodium bromide-bromate solution. Air blowing process flow sheet is shown in Fig 1.

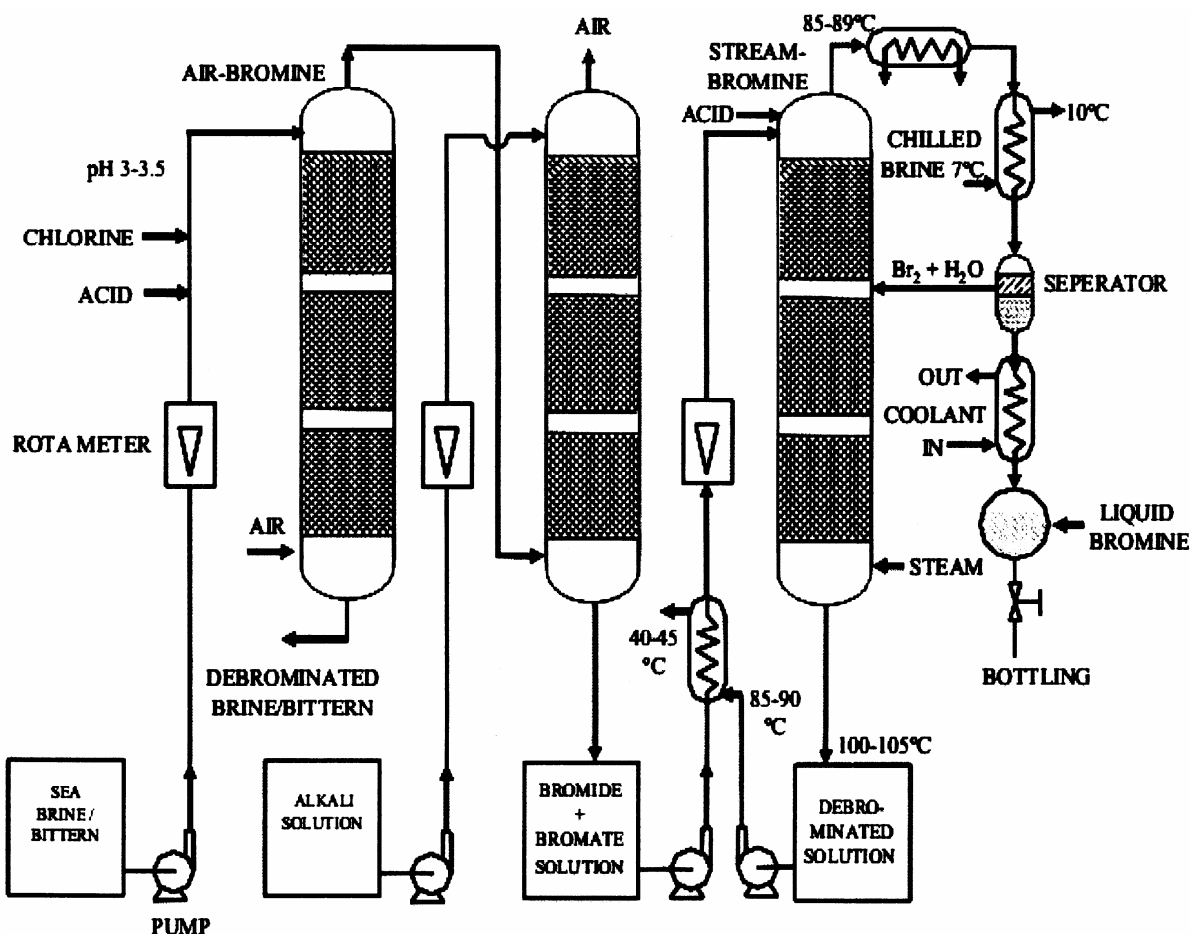


Fig.1—Air blowing process flow sheet

Model development

Wagner *et al.*²⁷ developed a model for the prediction and correlation of mass-transfer rates in distillation columns containing random packings using height equivalent to a theoretical plate concept and considering gas phase resistance as the controlling resistance. In the present study, the same model is adopted for desorption of bromine from solutions containing bromide bromate salts with appropriate changes for liquid phase as the controlling phase for mass-transfer. The height of an overall transfer unit HTU_L includes individual phase mass transfer coefficients and concentration difference as driving force and is defined as:

$$HTU_L = H_{iL} + (L/mG) H_{iG} \\ = (u_L/k_L \cdot a_e) [1 + (L/mG) (u_G k_L/u_L k_G)] \quad \dots (1)$$

The above equation is having three unknowns: the liquid and gas-side mass-transfer coefficients k_L and k_G ; and effective interfacial area a_e . The penetration

theory of Higbie²⁵ was further extended by Lockett and Placka²⁸ by introducing an enhancement factor ϕ to account for turbulent diffusion and multiple surface resistances as controlling one. Adopting the same line of action in the present study important equations were deduced as under:

$$k_L = (4 \phi_L D_L u_L / \pi h \chi)^{0.5} \quad \dots (2)$$

$$k_G = (4 \phi_G D_G u_G / \pi (\epsilon - h) \chi)^{0.5} \quad \dots (3)$$

At column operating conditions the enhancement factors can approximately be set equal to unity, so that only the value of the characteristic length χ must be determined in order to calculate the mass-transfer coefficients.

Wagner *et al.*²⁷ followed pressure drop model of Stichlmair *et al.*⁷ and derived following expression for the total interfacial area in wetted packing.

$$a_{tot}/a_p = [(1 - \epsilon + h)/(1 - \epsilon)]^{0.66} \quad \dots (4)$$

The total surface area in the irrigated column is expected to be greater than the effective interfacial area for mass-transfer, thus they proposed:

$$a_e/a_p = [(1 - \varepsilon + h)/(1 - \varepsilon)]^{2/3} - \alpha \quad \dots (5)$$

The term α takes into account the dry or ineffective part of the total surface area in the wetted packing and can be deduced from experimental data. The liquid holdup in the above expressions is calculated using Castillo *et al.*¹⁴ correlation which takes into account physical properties of liquid stream also.

Wagner *et al.*²⁷ observed that physical properties of liquid have little or no effect on the term $a_e/\chi^{0.5}$, while the packing height seems to have a pivotal influence on the mass-transfer. Based on this observation the characteristic length χ is expressed as²⁷:

$$\chi = C_{pk}^2 Z \quad \dots (6)$$

where C_{pk} is a dimensionless packing characteristic, which is constant for each packing and Z is the packed bed height. Value of packing characteristic for Rasching Ring packing has been given by Wagner *et al.* for 15-55 mm size packing and it varies from 0.028-0.067. In the present study, this value has been assumed as 0.061 arbitrarily to show comparison between the measured and calculated effective interfacial area for some packings by Wagner *et al.*²⁷. Substituting these values in the expressions for mass transfer coefficients, individual mass transfer coefficients were calculated followed by overall liquid side mass transfer coefficient.

For desorption of sparingly soluble solute in randomly packed column, substituting Eq. (2)-(6) into Eq. (1) described above, expression for height of transfer unit becomes:

$$(HTU)_{OL} = [(\pi.h.u_L)/(4.D_L)]^{0.5} [1 + (L/mG) \{(D_L.u_G.(\varepsilon - h))/(h.D_G.u_L)\}^{0.5}] [C_{pk}^2.Z^{0.5}/a_p] [\{(1 - \varepsilon + h)/(1 - \varepsilon)\}^{2/3} - 1]^{-1} \quad \dots (7)$$

Experimental Procedure

In the developmental study on air-blowing process, a glass column of 10 cm diameter filled with Rasching Ring packing of 1.25 cm size was used to collect data on desorption of bromine from seawater. A single nozzle of 1.25 cm diameter made from tube was placed centrally at the top as liquid distributor. Seawater to be processed was acidified to a pH of 3-3.5 before feeding in the tower. Chlorine gas was injected in the seawater feed line and air was blown

through an inlet of 1.9 cm diameter glass tube at the bottom of the tower. Orifice meter and area displacement type rotameters having $\pm 5\%$ error were used to measure flow rates of air and seawater, respectively. All experiments were carried out at ambient temperature (30°C) and hence effect of temperature on air requirement for stripping of bromine was not studied.

Experimental investigation has been carried out on stripping of bromine from aqueous solution of sodium bromide-bromate mixture of known concentration (40-66 g/L bromine) by acidification and steaming out using glass column of 6.25 cm diameter filled with 9.52 mm rasching ring packings upto 43.2 - 54 cm packed height. The effects of variables such as concentration of bromine in the solution, liquor and gas flow rates and different packed heights are studied. Bromine content in liquid samples is analyzed by the method of Willard and Hynes²⁹. Sodium bromide-bromate solution and acid entered the top of the column at room temperature (28-32°C) and live steam at 110°C at the bottom of the column. It was observed that the incoming solution attained boiling point temperature within a few centimeters of packed height and hence, uniform temperature was achieved across the column. Typical experimental data are presented in Table 1.

Based on dilution in magnesium ion content in the effluent compared to feed solution, steam consumption was calculated by the formula³⁰ in case of sodium bromide-bromate experiments:

$$C_1 * V_1 = C_2 * V_2 \quad \dots (8)$$

where C_1 and C_2 are concentration of Mg^{+2} in feed and effluent, respectively and V_2 is volume of effluent corresponding to V_1 volume of feed. Difference between V_2 and V_1 indicates steam consumption corresponding to V_1 volume of feed. Live steam utilized in pre-heating the feed solution gets condensed and comes down the column as part of the effluent. This amount was considered as a part of liquid loading in the column. It was assumed that about ten percent of inlet steam leaves the tower along with bromine. Liquid and acid flow rates were monitored by area displacement type rotameters having $\pm 5\%$ error.

Results and Discussion

Physical properties of liquid and gas streams and diffusivity of bromine in water, bittern and steam are

Table 1— Experimental observations and overall mass-transfer coefficient

U_L (m/s)	U_G (m/s)	X_{in}	X_{out}	L/mG	NTU	HTU (m)	$K_L a_{obs}$
Sea water							
Packed height 0.91 (m)							
0.0007	0.1163	0.0008	0.0003	0.0896	0.8863	1.0267	0.00065
0.0006	0.0664	0.0008	0.0003	0.1455	0.8877	1.0251	0.00060
0.0009	0.0996	0.0010	0.0002	0.1439	1.5061	0.6042	0.00152
0.0009	0.0581	0.0009	0.0002	0.2442	1.5678	0.5804	0.00157
0.0006	0.0581	0.0008	0.0002	0.1558	1.4049	0.6477	0.00090
0.0005	0.0415	0.0008	0.0002	0.2036	1.5857	0.5739	0.00094
0.0008	0.0166	0.0008	0.0002	0.7545	2.3163	0.3929	0.00204
0.0008	0.1329	0.0007	0.0002	0.0943	1.4936	0.6093	0.00132
0.0009	0.1163	0.0009	0.0002	0.1208	1.4987	0.6072	0.00148
Packed height 1.22 (m)							
0.0006	0.0664	0.0008	0.0002	0.1364	1.4989	0.8139	0.0007
0.0005	0.1827	0.0006	0.00001	0.0455	2.3701	0.5147	0.0010
0.0007	0.0498	0.0006	0.00001	0.2091	2.2358	0.5456	0.0012
0.0004	0.2242	0.0008	0.0001	0.0303	1.9263	0.6333	0.0007
0.0008	0.1993	0.0008	0.0001	0.0614	2.0982	0.5814	0.0013
0.0008	0.0415	0.0008	0.0001	0.3127	2.1434	0.5692	0.0015
0.0009	0.0249	0.0009	0.0002	0.5697	2.6887	0.4538	0.0020
0.0009	0.0581	0.0007	0.0001	0.2312	2.1406	0.5699	0.0015
0.0008	0.1163	0.0009	0.0001	0.1117	2.0024	0.6093	0.0014
Packed height 1.524 (m)							
0.0021	0.0581	0.0008	0.00006	0.5480	4.0362	0.3776	0.0054
0.0010	0.0249	0.0008	0.00008	0.6362	4.0253	0.3786	0.0027
0.0015	0.0498	0.0009	0.00008	0.4788	3.5775	0.4260	0.0036
0.0041	0.0747	0.0007	0.00006	0.8505	6.7745	0.2250	0.0181
0.0062	0.1080	0.0007	0.00001	0.8839	6.319	0.2412	0.0253
0.0072	0.1163	0.0008	0.00007	0.9597	8.2298	0.1852	0.0386
0.0086	0.1495	0.0006	0.00006	0.8889	6.8676	0.2219	0.0383
0.0095	0.1744	0.0008	0.00007	0.8459	6.0795	0.2507	0.0377
0.0120	0.2076	0.0003	0.00008	0.8967	2.6134	0.5832	0.0204
Sodium bromide-bromate solution							
Packed height 0.54 (m)							
0.0022	0.4595	0.0051	0.0001	0.0283	4.0568	0.1331	0.01633
0.0018	0.3998	0.0051	0.0001	0.0270	3.9941	0.135198	0.01336
0.0017	0.3249	0.0067	0.0002	0.0319	3.4709	0.1556	0.01115
0.0015	0.3384	0.0061	0.0004	0.0267	2.8858	0.1871	0.00807
0.0018	0.3953	0.0071	0.0003	0.0278	3.2704	0.1651	0.01113
0.0014	0.3144	0.0078	0.0008	0.0272	2.3333	0.2314	0.00617
0.0021	0.4522	0.0051	0.0001	0.0275	4.2540	0.1269	0.01640
Packed height 0.48 (m)							
0.0017	0.3893	0.0051	0.0002	0.0266	3.2533	0.1483	0.01170
0.0020	0.4147	0.0061	0.0006	0.0283	2.3328	0.2068	0.00947
0.0014	0.3159	0.0071	0.0002	0.0270	3.5013	0.1378	0.01037
0.0026	0.4321	0.0078	0.0010	0.0367	2.1315	0.2264	0.01172
Packed height 0.43 (m)							
0.0014	0.3099	0.0051	0.0006	0.0276	2.1948	0.1968	0.00726
0.0017	0.3668	0.0061	0.0009	0.0275	1.9349	0.2233	0.00754
0.0019	0.4147	0.0071	0.0012	0.0278	1.8242	0.2368	0.00814
0.0017	0.3758	0.0078	0.0014	0.0279	1.7041	0.2535	0.00692

given in Table 2 and equations used for calculation of mass transfer are given in Table 3. Regarding hydrodynamic calculations for packed column, equations given by Castillo *et al.* are used with the help of Excel Microsoft spread sheet. Slope of equilibrium curve, i.e. Henry's constant³¹ used for calculation is 55 and 286 for sea water and sodium bromide-bromate solution, respectively. Models presented by Onda *et al.* and Wagner *et al.* have been applied to experimental data given in Table 1 and calculated results are given in Table 3.

By rearranging formulas for liquid phase mass transfer coefficient given in Table 3, liquid phase volumetric mass transfer coefficient is calculated as per the following formula:

$$K_L a = [a_e(m.k_L.k_G)/(m.k_G + k_L)] \quad \dots (9)$$

Table 2— Physical properties of liquid-gas streams and diffusivity of bromine in water and steam

Notation	Units	Value
ρ_L	kg/m ³	1025 for sea water
ρ_L	kg/m ³	1035 for sodium bromate solution
ρ_G	kg/m ³	0.605 for steam
ρ_G	kg/m ³	1.2041 for air
μ_L	kg/m.s	0.00029 E-4 for sea water sodium bromide and bromate solution
μ_G	kg/m.s	1.7 E -5 for steam
μ_G	kg/m.s	1.983 E -5 for air
σ	N/m	0.059 for sea water sodium bromide and bromate solution
D_L	m ² /s	2.10 E-9 for sea water sodium bromide and bromate solution
D_G	m ² /s	6.2 E-5 for steam
D_G	m ² /s	1.21 E -5 for air

Table 3— Equations used for mass-transfer calculations

Onda <i>et al.</i> model	
1	$k_G = 5.23 D_G a_p (\rho_G u_G / a_p \mu_G)^{0.7} (Sc_G)^{1/3} (a_p d_p)^{-2}$
2	$k_L = 0.0051 (\mu_L g / \rho_L)^{1/3} (u_L \rho_L / a_p \mu_L)^{2/3} (D_L \rho_L / \mu_L)^{1/2} (a_p d_p)^{0.4}$
3	$a_e / a_p = 1 - \exp[-1.45 (\sigma_c / \sigma_i)^{0.75} (Re_i)^{0.1} (We_i)^{0.2} (Fr_i)^{0.05}]$
4	$Re_i = u_i \rho_i / a_p \mu_L$
5	$We_i = u_i^2 \rho_i / \sigma_i a_p$
6	$Fr_i = u_i^2 a_p / g$
Wagner <i>et al.</i> model	
7	$k_L = (4 \phi_L D_L u / \pi h \chi)^{0.5}$
8	$k_G = (4 \phi_G D_G u_G / \pi (\epsilon - h) \chi)^{0.5}$
9	$a_e / a_p = [(1 - \epsilon + h) / (1 - \epsilon)]^{2/3} - \alpha$
10	$\chi = C_{pk}^2 Z$
11	$1/K_L a = (1/a_e) [1/k_L + 1/mk_G]$
12	$HTU = u_i / K_L a$
13	$NTU = \{\lambda / (\lambda - 1)\} \ln \{[(\lambda - 1) / \lambda] (X_{in} / X_{out}) + (1/\lambda)\}$
14	$\lambda = mG/L$

Diffusivity of bromine in steam and brine is of the order of 10⁻⁵ and 10⁻⁹ respectively as calculated based on the available correlations³². Considering these values of diffusivity of bromine, the above formula can be simplified as under:

$$K_L a = a_e.k_L \text{ (for } D_L \lll D_G) \quad \dots (10)$$

Thus, liquid phase mass transfer coefficient is the overall mass transfer resistance in stripping of bromine from sea water and bromide bromate solution. Thus, the calculated value of liquid phase volumetric mass transfer coefficient depends only on two parameters, namely effective interfacial area between liquid and gas phase and liquid film mass transfer coefficient.

Effective interfacial area

Effective interfacial area for the experimental data has been calculated for Onda *et al.* and Wagner *et al.* correlations and results are given for stripping of bromine from sea water and bromide bromate solution in Table 4. It can be seen that effective interfacial area increases with increasing liquid flow rate which in turn increases the liquid hold up in the column. Interfacial area is lower for Wagner correlation compared to Onda correlation for stripping of bromine from sea water and bromide-bromate solution. It may be noted that Wagner correlation for interfacial area is based on liquid hold up in the tower whereas, Onda correlation is based on dimensional numbers like Weber, Froude and Renolds numbers. This appears to be the determining factor for lower values of a_e for Wagner correlation. Estimation of effective interfacial area in packed bed for liquid desiccant contactors has been studied by Gandhidasan³³ considering three correlations proposed by Shulman *et al.*²⁰, Onda *et al.*^{3,4} and Shi and Mersmann²⁴. It is reported that interfacial area increases with increasing liquid flow rate and for Onda *et al.* correlation the value was the highest and for Shi and Mersmann correlation it was the lowest. These observations tally with the values reported in the present study.

Liquid film mass transfer coefficient

Liquid film mass transfer coefficient is calculated based on correlations given in Table 3 for experimental observations given in Table 1 and results are given in Table 4. It can be seen that value of liquid phase mass transfer coefficient based on Onda correlation is lower compared to that of Wagner

Table 4— Values of effective interfacial area and calculated liquid film mass transfer coefficient for debromination of sea water and sodium bromide-bromate solution.

L (kg/sm ²)	Interfacial area (a_e)		Liquid film mass transfer coefficient $k_L \times 10^4$		Overall liquid phase mass transfer coefficient $K_L a \times 10^4$	
	Onda <i>et al.</i>	Wagner <i>et al.</i>	Onda <i>et al.</i>	Wagner <i>et al.</i>	Onda <i>et al.</i>	Wagner <i>et al.</i>
Sea water						
Packed height 0.91 (m)						
0.69	38.19	9.71	0.30	1.89	11.59	18.34
0.64	37.12	9.24	0.29	1.86	10.72	17.24
0.95	43.08	11.98	0.38	1.99	16.19	23.88
0.94	42.91	11.89	0.37	1.99	16.01	23.67
0.6	36.22	8.86	0.28	1.84	10.02	16.34
0.56	35.28	8.47	0.26	1.82	9.32	15.44
0.83	40.95	10.96	0.34	1.95	14.06	21.36
0.83	40.95	10.96	0.34	1.95	14.06	21.36
0.93	42.74	11.81	0.37	1.99	15.83	23.46
Packed height 1.22 (m)						
0.6	36.22	8.86	0.28	1.84	10.02	16.34
0.55	35.04	8.37	0.26	1.82	9.15	15.21
0.69	38.19	9.71	0.30	1.89	11.59	18.34
0.45	32.46	7.34	0.23	1.76	7.41	12.88
0.81	40.57	10.79	0.34	1.94	13.71	20.94
0.86	41.50	11.22	0.35	1.96	14.59	22.00
0.94	42.91	11.89	0.37	1.99	16.01	23.67
0.89	42.04	11.47	0.36	1.97	15.12	22.63
0.86	41.50	11.22	0.35	1.96	14.59	22.00
Packed height 1.524 (m)						
2.11	57.93	20.17	0.64	2.28	37.05	46.05
1.05	44.73	12.79	0.40	2.03	17.96	25.93
1.58	52.07	16.70	0.53	2.17	27.46	36.31
4.21	74.35	31.58	1.01	2.57	75.36	81.09
6.32	85.80	41.04	1.33	2.75	114.01	112.92
7.39	90.58	45.37	1.48	2.83	133.60	128.21
8.8	96.19	50.74	1.66	2.91	159.38	147.71
9.77	99.67	54.24	1.78	2.96	177.08	160.74
12.33	107.80	62.91	2.07	3.08	223.65	193.93
Sodium bromide-bromate solution						
Packed height 0.54 (m)						
2.25	191.07	46.27	0.95	0.54	181.33	24.9
1.87	180.22	40.58	0.87	0.52	157.18	21.3
1.80	177.91	39.24	0.86	0.52	152.36	20.5
1.56	170.15	35.89	0.80	0.51	136.86	18.3
1.90	181.18	41.01	0.88	0.53	159.24	21.6
1.48	167.10	34.55	0.78	0.51	131.09	17.5
2.15	188.50	44.91	0.93	0.54	175.39	24.0

(Contd)—

Table 4— Values of effective interfacial area and calculated liquid film mass transfer coefficient for debromination of sea water and sodium bromide-bromate solution.— (Contd)

L (kg/sm ²)	Interfacial area (a_e)		Liquid film mass transfer coefficient $k_L \times 10^4$		Overall liquid phase mass transfer coefficient $K_L a \times 10^4$	
	Onda <i>et al.</i>	Wagner <i>et al.</i>	Onda <i>et al.</i>	Wagner <i>et al.</i>	Onda <i>et al.</i>	Wagner <i>et al.</i>
Packed height 0.48 (m)						
1.80	177.91	39.47	0.86	0.54	152.36	21.2
2.03	184.93	42.89	0.91	0.55	167.38	23.5
1.48	167.10	34.53	0.78	0.52	131.09	18.0
2.75	203.25	52.31	1.04	0.57	211.42	30.1
Packed height 0.43 (m)						
1.48	167.10	34.52	0.78	0.54	131.09	18.5
1.74	176.22	38.56	0.84	0.55	148.88	21.2
2.00	184.01	42.34	0.90	0.56	165.35	23.8
1.82	178.57	39.65	0.86	0.55	153.74	22.0

for stripping of bromine from sea water. Value of k_L varies from 0.23×10^{-4} to 2.07×10^{-4} for Onda correlation and 1.76×10^{-4} to 3.08×10^{-4} for Wagner correlation. For bromide bromate solution value of k_L is smaller in case of Wagner compared to that of Onda correlation, though the difference is not significant. In both these correlations, exponent of D_L is 0.50 and value of $(D_L)^{0.5}$ decides the value of liquid phase mass transfer coefficient. Contribution of other parameters is less. This could be one of the reasons for lower value of liquid phase mass transfer coefficient based on Onda correlation. Above values indicate that in general above correlations give comparable value of liquid phase mass transfer coefficient within limitations of operating parameters and measurement of process parameters.

Overall volumetric liquid phase mass transfer coefficient

Overall volumetric liquid phase mass transfer coefficient is calculated using Eq. (9) with the value of calculated interfacial area given in Table 4. The deviation between experimental and calculated volumetric liquid phase mass transfer coefficient was defined as under:

$$\text{Deviation in \%} = \left\{ \frac{\text{Abs} (K_L a_{\text{exp}} - K_L a_{\text{calc.}})}{K_L a_{\text{exp}}} \right\} \times 100 \dots (11)$$

Value of percentage deviation provides a measure of the quality of the model. The average deviation for overall volumetric liquid phase mass transfer coefficient calculated using Eq. (9) for observations given in Table 1 varies from 5-46% for sea water data based on Onda correlation and 36-54% for Wagner

correlations. In case of Onda correlations for packed height 0.91 and 1.22 m deviation is almost similar 5-6%, whereas for Wagner correlation it is comparable for all three packed height studied. For bromide-bromate solution average deviation varies from 10-25% for Onda correlation and 83-86% for Wagner correlation. This shows that experimental data correlate better with the help of Onda correlation than Wagner. Wagner *et al.* tested their model using 326 experimental data points taken on six different systems involving organic solvents under various conditions. They observed that 90% of the predicted values showed a deviation of less than 10% from the experimental observations. Compared to this, based on the present study, it is evident that Wagner model is not satisfactorily applicable to aqueous systems like sea brines.

Similar exercise was carried by Castillo *et al.* for removal of volatile organic compounds (VOCs) by steam stripping from water. Their results indicated 29% average deviation for the overall volumetric mass transfer coefficients based on the liquid phase and 23% deviation in the packed height of the column. In the present study average deviation observed in case of stripping of bromide bromate solution based on Onda correlation is better than that of Castillo *et al.* results, but it is higher when analyzed based on Wagner correlation.

Observed value of volumetric liquid phase mass transfer coefficient is plotted against calculated value for debromination of sea water and bromide-bromate solution and plots are shown in Figs 2-6. Figures 2 and 3 show that for Onda and Wagner correlations

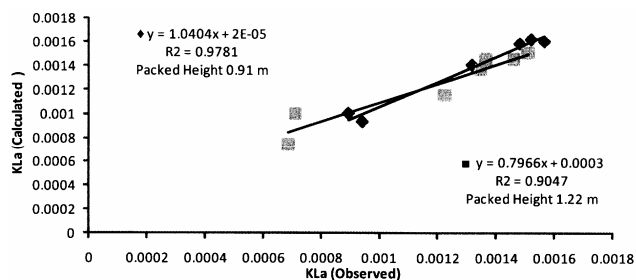


Fig. 2—Experimental versus predicted volumetric liquid phase mass transfer coefficient for debromination of sea water based on Onda *et al.*^{4,5} correlation

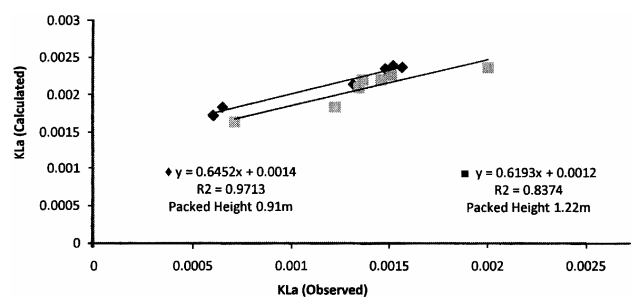


Fig. 3—Experimental versus predicted volumetric liquid phase mass transfer coefficient for debromination of sea water based on Wagner *et al.*²⁷ correlation

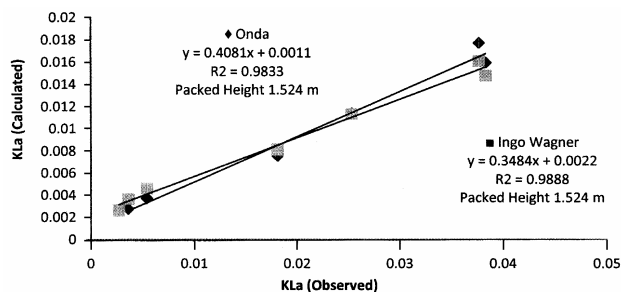


Fig. 4—Experimental versus predicted volumetric liquid phase mass transfer coefficient for debromination of sea water based on Onda *et al.*^{4,5} and Wagner *et al.*²⁷ correlation

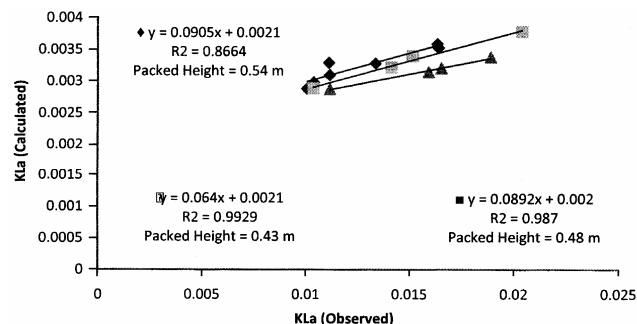


Fig 5— Experimental versus predicted volumetric liquid phase mass transfer coefficient for debromination of sodium bromide-bromate solution based on Onda *et al.*^{4,5} correlation

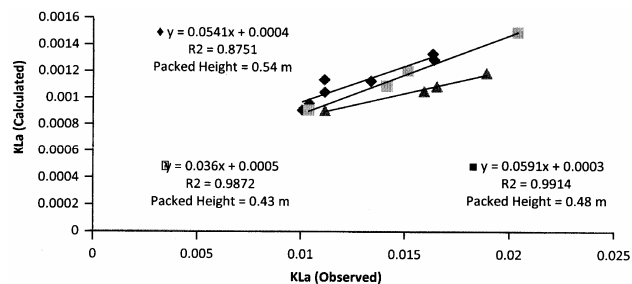


Fig. 6—Experimental versus predicted volumetric liquid phase mass transfer coefficient for debromination of sodium bromide-bromate solution based on Wagner *et al.*²⁷ correlation

trend is almost identical for debromination of sea water for packed heights of 0.91 and 1.22 m with good correlation coefficient whereas Fig 4 shows that Onda and Wagner correlation exhibits identical behaviour for debromination of sea water with 1.524 m packed height with identical correlation coefficient. In case of debromination of bromide-bromate solution, Onda and Wagner correlations show identical behaviour for all three packed height studied. These plots show expected improvement with respect to increase in packed height.

Castillo *et al.* observed that there is an effect of the operating conditions such that for $K_L a < 0.004$ (1/s), their method over predicted mass transfer coefficients while at higher values ($K_L a > 0.004$) the method under predicted mass transfer coefficient. In the present study this type of trend is not evident. Observed values of volumetric liquid phase mass transfer coefficient is lower than that of calculated values for debromination of sea water based on Onda and Wagner correlations for packed heights of 0.91 and 1.22 m. But this trend is reverse for packed height 1.524 m. In case of debromination of bromide-bromate solution the observed value of mass transfer coefficient is lower than calculated value based on Onda correlation, but in case of Wagner correlation this trend is reverse for all packed height studied.

Results of Castillo *et al.* indicate values of volumetric liquid phase mass transfer coefficient in the range of 0.001-0.008 (1/s) whereas in the present study it varies from 0.0006-0.0164 (1/s), in other words, steam stripping of bromine from aqueous systems is comparatively easier than stripping of VOCs from water.

Height of transfer unit and overall liquid phase mass transfer coefficient

The Eq. (7) for desorption of sparingly soluble solute (bromine) in randomly packed column height of transfer unit is given by:

Table 5— Calculation of HTU and K_La based on modified model of Wagner *et al.* for debromination of sea water and bromide-bromate solution

HTU_{calc} (m)	K_La_{calc}	HTU_{obs} (m)	K_La_{obs}	Deviation (%)	
				HTU	K_La
Sea water					
Packed height 0.91 (m)					
0.3610	0.0019	1.0267	0.0006	64.8	187.2
0.3563	0.0018	1.02514	0.0006	65.2	190.6
0.3817	0.0024	0.6042	0.0015	36.8	59.8
0.3810	0.0024	0.5804	0.0016	34.3	53.8
0.3523	0.0017	0.6477	0.0009	45.6	85.7
0.3481	0.0016	0.5739	0.0009	39.3	66.5
0.3728	0.0022	0.3929	0.0020	5.1	6.4
0.3728	0.0022	0.6093	0.0013	38.8	65.0
0.3803	0.0024	0.6072	0.0015	37.4	61.2
Packed height 1.22 (m)					
0.4079	0.0014	0.8139	0.0007	49.9	129.4
0.4018	0.0013	0.5147	0.0010	21.9	47.3
0.4179	0.0016	0.5457	0.0012	23.4	50.1
0.3880	0.0011	0.6333	0.0007	38.7	87.7
0.4298	0.0018	0.5814	0.0013	26.1	55.6
0.4343	0.0019	0.5692	0.0015	23.7	50.7
0.4411	0.0020	0.45376	0.0020	2.8	18.2
0.4369	0.0020	0.5699	0.0015	23.3	49.9
0.4343	0.0019	0.6093	0.00136	28.7	61.3
Packed height 1.524 (m)					
0.5689	0.0046	0.3776	0.0054	50.7	14.7
0.5027	0.0026	0.3786	0.0027	32.8	3.2
0.5403	0.0036	0.4260	0.0036	26.8	1.3
0.6446	0.0081	0.2250	0.0181	186.5	55.2
0.6949	0.0113	0.2412	0.0253	188.1	55.4
0.7156	0.0128	0.1852	0.0386	286.5	66.7
0.7397	0.0148	0.2219	0.0383	233.3	61.4
0.7547	0.0161	0.2507	0.0377	201.1	57.3
0.7894	0.0194	0.5832	0.0204	29.4	5.1
Sodium bromide-bromate solution					
Packed height 0.54 (m)					
0.168	0.0129	0.133	0.0163	26.2	20.1
0.163	0.0111	0.135	0.0133	20.8	17.2
0.163	0.0106	0.156	0.0112	4.7	4.5
0.159	0.0095	0.145	0.0104	9.3	8.5
0.164	0.0112	0.165	0.0111	0.7	0.7
0.157	0.0091	0.142	0.0101	10.8	9.7
0.167	0.0125	0.127	0.0164	31.4	23.9
Packed height 0.48 (m)					
0.153	0.0113	0.123	0.0141	24.8	19.9
0.156	0.0125	0.129	0.0151	20.9	17.3
0.149	0.0096	0.138	0.0104	8.0	7.4
0.165	0.0161	0.130	0.0204	27.1	21.3
Packed height 0.43 (m)					
0.141	0.0101	0.128	0.0112	10.0	9.1
0.145	0.0116	0.106	0.0159	36.8	26.9
0.148	0.0130	0.102	0.0189	44.9	31.0
0.146	0.0120	0.106	0.0165	37.2	27.1

$$(HTU)_{OL} = [(\pi.h.u_L)/(4.D_L)]^{0.5} [1 + (L/mG) \{(D_L.u_G.(\epsilon - h))/(h.D_G.u_L)\}^{0.5}][C_{pk} .Z^{0.5}/a_p] [\{(1 - \epsilon + h)/(1 - \epsilon)\}^{2/3} - 1]^{-1} \dots (12)$$

The model has been applied to experimental data given in Table 1 and calculated results are compared with the experimental findings as shown in Table 5. Average percentage deviation between observed and calculated value of HTU is 23-34% for stripping of bromine from sea water and 14-32% from bromide-bromate solution. Wagner observed that the best agreement was for the high efficiency packings, 90% of the analyzed data showed deviation less than 10%. Thus, the above results show that the data collected on aqueous systems also fit satisfactorily. Using value of calculated HTU, overall volumetric liquid phase mass transfer coefficient was calculated by following Eq.:

$$K_La = u_L/HTU \dots (13)$$

It can be seen from values of mass transfer coefficient given in Table 5 that average percentage deviation is 35-57% for debromination of sea water and 12-24% for debromination of bromide bromate solution. These values are comparable with results obtained by Eq. (9).

Conclusion

Model proposed by Wagner for distillation data considering gas phase resistance as the controlling resistance is modified in the present study for liquid phase as the controlling phase for mass-transfer and successfully applied to the experimental data collected during process developmental study for recovery of bromine from brine by air blowing method. Experimental data collected on debromination of sodium bromide-bromate mixture are evaluated based on the Onda *et al.* and Wagner *et al.* model. Calculated values of liquid phase mass transfer coefficient synchronize well with the observed values of liquid phase mass transfer coefficient for debromination of sea water and bromide bromate solution.

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Nomenclature

a_e	: Specific effective interfacial area (m^2/m^3)
a_p	: Specific packing surface area (m^2/m^3)
a_{tot}	: Specific total surface area (m^2/m^3)
C_{pk}	: Packing characteristic
D_L	: Liquid diffusion coefficient (m^2/s)
d_p	: Particle diameter $d_p = 6(1 - \epsilon)a_p^{-1}$ (m)
D_v	: Vapor diffusion coefficient (m^2/s)
G	: Gas (Vapour) flow rate ($\text{kg}/\text{s} \cdot \text{m}^2$)
h	: Operational holdup (m^3/m^3)
h_0	: Operational holdup under loading point (m^3/m^3)
H_{tG}	: Height of a transfer unit based on gas phase resistance (m)
H_{tL}	: Height of a transfer unit based on liquid phase resistance (m)
HTU_L	: Overall height of transfer unit based on liquid phase
k_L	: Liquid-side mass-transfer coefficient (m/s)
k_V	: Vapor-side mass-transfer coefficient (m/s)
L	: Liquid flow rate ($\text{kg}/\text{s} \cdot \text{m}^2$)
m	: Slope of equilibrium line
u_L	: Liquid velocity (m/s)
u_V	: Vapor velocity (m/s)
Z	: Packed-bed height (m)
	Greek Letters
α	: Ineffective part of the total surface area in a wetted packing
ϵ	: Void fraction (m^3/m^3)
μ_L	: Liquid viscosity (centi poise)
μ_V	: Vapor viscosity (centi poise)
ρ_L	: Liquid density (kg/m^3)
ρ_V	: Gas (Vapor) density (kg/m^3)
τ_L	: Exposure time of liquid element to vapor phase (s)
τ_V	: Exposure time of liquid element to liquid phase (s)
ϕ_L	: Liquid phase enhancement factor for turbulent diffusion
ϕ_V	: Vapor enhancement factor for turbulent diffusion
χ	: Characteristic length (m)

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