ACKNOWLEDGMENT

The assistance of M. Baugh and K. Smith in the generation of the experimental data reported herein is gratefully acknowledged. The authors also wish to thank Professor J. M. Prausnitz for his generous assistance and enthusiastic encouragement in the development of the thermodynamic treatment.

NOTATION

a_A, a_A^* = activity and activity in saturated solution of solute A, respectively

A_m = diffusional area of the membrane, cm^2

C, C^* = concentration and saturation concentration of solute in liquid, respectively, μg/cm^3

C_A, C_A^* = concentration and saturation concentration of solute A in polymer, respectively, μg/cm^3

C_d = solute concentration in the downstream compartment, μg/cm^3

C_s = solubility of solute in liquid, μg/cm^3

D = diffusivity, cm^2/s

f_A = fugacity of solute, A

ΔG, $\Delta \overline{G}$ = the change in molar and partial molar free energy respectively

ΔH_f = heat of fusion, K cal/mole

J = steady state flux, μg/cm^2 s

K = partition coefficient of solute between polymer and solution, or permeation cell constant

l = membrane thickness, cm

L = lag-time of the diffusion experiment

M_A = molecular weight of solute, A

M_t = amount of penetrant present in the downstream compartment at time, t

R = gas constant, cal/mole °K

ΔS_f = entropy of fusion, cal/mole °K

T_M = melting point of crystalline solid, °K

T = absolute temperature, °K

V_A, V_B = molar volume of solute A and solvent B, respectively, cm^3/mole

V_d = volume of liquid in the downstream compartment of the permeation cell

X_A, X_B = mole fraction of solute A and solvent B, respectively

Greek Letters

Γ_A, Γ_A^* = volume fraction normalized activity coefficient of solute A and the activity coefficient at saturation, respectively

γ_A, γ_A^* = mole fraction normalized activity coefficient of solute A and at saturation, respectively

δ_A, δ_P = solubility parameters of solute A and of polymer respectively, $[\text{cal/cm}^3]^{1/2}$

ρ_A = density of solute, g/cm^3

ϕ_A, ϕ_A^* = volume fraction of solute A in solution and the saturated volume fraction, respectively

ϕ_P, ϕ_P^* = volume fraction of polymer in solution and the saturated volume fraction, respectively

χ_{AP}, χ_{AB} = interaction parameter between solute A with polymer and with solvent, respectively

LITERATURE CITED

Barrer, R. M., Diffusion in and through Solids, Cambridge University Press, England (1955).

Daynes, H. A., *Proc. Roy. Soc.*, **A97**, 286 (1920).

Flory, P. J., *Principles of Polymer Chemistry*, pp. 513-514, Cornell University Press, Ithaca, N. Y. (1953).

Gardon, J. L., "Cohesive Energy Density," *Encyclopedia of Polymer Science and Technology*, Vol. 3, p. 884, Wiley, New York (1965).

Hildebrand, J. H., and R. L. Scott, *The Solubility of Nonelectrolytes*, 3 ed., Dover Publications, New York (1964).

Huggins, M. L., *J. Phys. Chem.*, **46**, 151 (1942).

Michaels, A. S., and H. J. Bixler, "Membrane Permeation: Theory and Practice," in *Progress in Separation and Purification*, E. S. Perry, ed., Vol. I, pp. 143-186, Interscience, New York (1968).

Small, P. A., *J. Appl. Chem.*, 3, 71 (1953).

Manuscript received April 17, 1975; revision received May 30, and accepted June 2, 1975.

Flooding Rates and Holdup in Packed Liquid-Liquid Extraction Columns

Countercurrent flow of liquids in columns packed with Raschig rings was studied with fluids having a wide range of physical properties. These results, along with data reported previously from other studies, were used to develop a correlation for predicting flooding rates in packed columns that is significantly better than previous correlations. Dispersed phase holdup in packed columns can be estimated over a wide range of flow rates or flow ratio by assuming a constant slip velocity between the two phases which is dependent on the properties of the fluids and packing used. Although the slip velocity is thus essentially constant at flow rates below flooding, the flooding rate correlation indicates that this term is not necessarily constant at flooding conditions.

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SCOPE

Previous studies of flooding rates and dispersed phase holdup in packed columns have been limited to conventional water-organic solvent systems, and correlations developed from these data are not reliable for predicting flooding rates for fluids with high density differences or with other physical properties far removed from conventional conditions. Additional flooding rate and holdup data have been obtained in this study by using mercury and glycerol solutions as well as water and carbon tetrachloride or dibromomethane. The data cover a wide range of physical properties. From these data and information obtained in previous studies, a new correlation has been developed to predict flooding rates, and a better understanding of holdup has been made possible. Since the new correlation is based on data covering a wider range of fluid properties, it should be more reliable for predicting performance of liquid-liquid extraction columns. In previous work, the effects of density difference were not adequately studied; that is, this parameter was only varied over a narrow range. Consequently, the earlier results were in disagreement relative to the effects of density difference on column behavior. In addition, they also failed to establish definite trends concerning the effects of other parameters such as viscosity and packing diameter. The additional new data include a range of values for all of these parameters and, therefore, can improve our understanding of their effects.

CONCLUSIONS AND SIGNIFICANCE

Flooding rates in liquid-liquid columns packed with Raschig rings can be predicted by

$$V_{c,f}^{1/2} + (0.844\Delta\rho^{0.145}\, d_p^{0.298}\, \mu_c^{-0.084}\, \epsilon^{-0.078})\, V_{d,f}^{1/2} = 23.8\Delta\rho^{0.269}\, d_p^{0.494}\, \mu_c^{-0.084}\, \epsilon^{0.5}$$

This equation has been developed from what is considered to be the best experimental data available from the present study and from earlier work. The correlation is based on the widest range of fluid properties yet studied and should be the most reliable relation for predicting packed column performance. The new relation is recommended especially for high-density difference systems ($\Delta\rho >> 0.5$ g/cm^3) and is significantly superior to correlations resulting from previous studies.

No attempt has been made to develop a similar correlation for Berl saddles or other types of packing because fewer data are available for these materials. However, the results from this study can be used to estimate flooding data for any similar packing shape, since the dependence on nominal packing size and fluid properties is likely to be comparable for other packing materials. Two or more measurements with a new packing type can be used to evaluate two coefficients in the correlation, and the resulting equation can be used to estimate performance for conditions of interest. This technique was tested for the limited amount of data available on Berl saddles, and the results were favorable.

For a given packing material, dispersed phase holdup can be correlated over a wide range of flow ratios by assuming that the two phases interact with a constant slip velocity. The slip velocity is a function of the fluids and packing used. When the dispersed phase holdup values are greater than 10%, this assumption of constant slip velocity appears to be more accurate than those usually proposed. However, a better understanding of holdup behavior is still needed.

In a recent paper by the authors (Watson and McNeese, 1973), the hydrodynamics of countercurrent flow of high-density (difference) fluids such as mercury and water in packed columns were shown to be significantly different from those observed with conventional organic solvents and water. Flooding rates and dispersed phase holdup with high-density fluids are not predicted reliably by correlations developed previously from measurements with organic-aqueous systems. For mercury-water systems, a simple correlation based on the assumption of a constant superficial slip velocity was shown to describe holdup and flooding rates. The effects of packing diameter and void fraction were evaluated; however, it was realized that these results were demonstrated only for the mercury-water system and did not necessarily apply over a wide range of fluid properties.

The need for data and correlations covering a wide range of physical properties, especially density difference, is apparent. A single correlation, applicable to both conventional low-density and high-density systems, is desirable. Such a correlation should provide more reliable predictions of column performance under new conditions of interest, especially when the conditions are far removed from those for conventional systems. The purpose of the present study was to provide additional hydrodynamic data and to develop an improved correlation. The experimental portion of the study included an evaluation of the effects of continuous phase viscosity for high-density (mercury-water) systems using glycerol solutions. In addition, measurements were made with selected systems comprised of water and organic fluids having relatively high densities (for example, CCl_4 and CH_2Br_2). These data provide a broader range of physical properties than has been available previously and, when used with existing data from conventional and high-density systems, permit the development of general correlations. Other parameters investigated in this study include packing diameter and packing void fraction.

EXPERIMENTAL

The equipment used in this study has been described previously (Watson and McNeese, 1973). Liquids flowing through the column, which was 5.08 cm (2 in.) ID × 61 cm (2 ft) long and packed with 0.953 cm (3/8 in.) Raschig rings, could be isolated for holdup measurements by suddenly and simultaneously closing ball valves located at each end of the column. The column diameter to packing diameter ratio was only 5.3. A higher ratio (8 or greater) was desired, but the supply of mercury and the pumping capacity would not permit larger columns. The previous study suggested that wall effects were small for these conditions. The dispersed (heavy) phase was pumped and metered by a CPS-3 diaphragm pump manufactured by the Lapp Insulator Company. The continuous phase was circulated through the column with a small centrifugal pump and metered by rotameters. The principal modification made to the equipment involved addition of devices for recirculating the continuous (as well as the dispersed) phase and for removing heat that was added to the liquids by the pumps. A water cooled heat exchanger was installed in the continuous phase piping, and temperatures were maintained within approximately ± 1/2° C of the desired value by manually adjusting the cooling water flow rate.

Flooding measurements were made by using the procedure employed in the earlier study (Watson and McNeese, 1973). Flow rates of the phases were slowly increased until they could no longer be maintained at a constant value with a constant pressure drop. When the column could be operated at steady conditions for more than 15 min., it was considered to be nonflooded. This procedure appeared to be more quantitative and more reproducible than methods based on visual observations, although sharply defined flooding points are always difficult to determine.

The experiments with the mercury-glycerol system were made by using polyethylene packing from previous mercury-water experiments. However, this packing (as well as similar packing made of Teflon) was wet by the halocarbons (CCl_4 and CH_2Br_2) and showed evidence of swelling. For this reason, the use of porcelain packing was necessary in the experiments with the dense organic fluids. The porcelain packing was wet by the continuous (water) phase but not by the dispersed (halocarbon) phase.

The glycerol used in this study contained less than 0.5% total impurities. Viscosities of the glycerol solutions were measured with a Brookfield viscometer. Glycerol concentrations were used which correspond to viscosities up to 15 centipoise. Interfacial tension values for the CCl_4 and CH_2Br_2 were determined with a platinum-ring tensiometer.

FLOODING RESULTS

Typical flooding data obtained in the present study are summarized in Table 1 and are shown in Figures 1 and 2, where the square root of the continuous phase superficial velocity is plotted against the square root of the dispersed phase velocity. Conditions below and to the left of the data points represent nonflooded conditions; conditions above and to the right of the points represent flooded conditions. This type of plot frequently yields a straight line, and data from the mercury-water system could be correlated by a line having a slope of −1, which corresponds to a constant superficial slip velocity at flooding (Watson and McNeese, 1973). Plots of the data for glycerol and relatively dense organic fluids (see Figures 1 and 2) also form straight lines; however, the data are best represented by lines having slopes other than −1. Similar behavior has been reported for conventional low-density difference systems (Breckenfeld and Wilke, 1950; Crawford and Wilke, 1951; Ballard and Piret, 1950; and Dell and Pratt, 1951). Thus, it appears that the assumption of a constant superficial slip velocity suggested by the mercury-water study is not general, even for high-density systems.

DEVELOPMENT OF FLOODING CORRELATIONS

Results of the present and previous studies suggested that a general flooding correlation could be developed that is based on flooding curves having the form

$$V_{c,f}^{1/2} + k_1 V_{d,f}^{1/2} = k_2 \qquad (1)$$

where $V_{c,f}$ and $V_{d,f}$ are superficial velocities of continuous and dispersed fluids at flooding conditions, and k_1 and k_2 are constants determined by fluid and packing properties. This relation produces straight lines on a square-root plot such as Figure 1. All experimental data considered for this study were plotted in the manner shown in Figure 1, and the best linear fit to each data set was determined by a least-squares fit. Data from the literature were used in developing the final correlation only if the standard errors in k_1 and k_2 were less than 30% of their most probable value. This criterion eliminated several data sets, especially those consisting of only one or two flooding points for given fluids and packing size. The parameters k_1 and k_2 for each data set are summarized in Table 1. Although various packing materials have been investigated in previous studies, insufficient data are available to permit development of correlations covering a wide range of system parameters for packing shapes other than Raschig rings, and the data used were limited to this packing type.

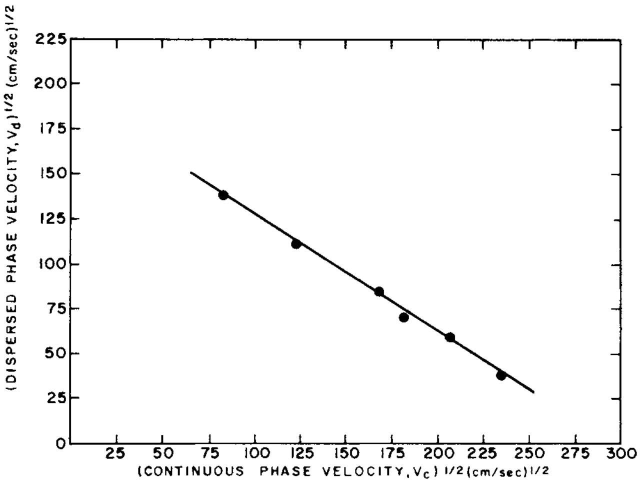

Fig. 1. Flooding rates for countercurrent flow of CH_2Br_2 with water through 0.953 cm (3/8 in.) Raschig rings.

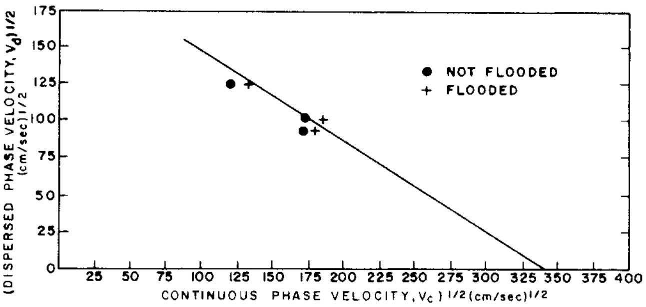

Fig. 2. Flooding rates for countercurrent flow of mercury with glycerol solution (15 centipoise) through 0.953 cm (3/8 in.) Raschig rings.

Each of the data sets could be described equally well by the two parameters k_1 and k_2 or by the intercepts of plots such as Figures 1 and 2, $V_{c,o}^{1/2}$ and $V_{d,o}^{1/2}$; either set of two parameters defines the least-squares line fitted to the data. Although the choice of parameters to use in studies of the effects of physical properties was arbitrary, we chose to work with the intercepts since we felt that physical interpretation of the results would be easier if the intercepts (rather than one intercept and slope) were used. The intercepts were assumed to be power functions of several parameters such as density difference $\Delta\rho$, packing diameter d_p, packing void fraction ϵ, continuous phase viscosity μ_c, and interfacial tension σ. That is

$$V_{d,o}^{1/2} = A_1 (\Delta\rho)^{a_1} d_p^{b_1} \epsilon^{c_1} \mu_c^{d_1}$$
$$V_{c,o}^{1/2} = A_2 (\Delta\rho)^{a_2} d_p^{b_2} \epsilon^{c_2} \mu_c^{d_2}$$

The coefficients and exponents in these equations were evaluated by linear regressions of the logarithms of these variables, that is, a logarithmic fit. Correlations were made with all of the terms listed and also with some terms ignored. The correlations were compared by using the F ratio as a figure of merit:

TABLE 1. SUMMARY OF AVAILABLE FLOODING DATA

Packing diameter (cm)	Fluids	Void fraction	Viscosity of continuous phase (centipoise)	Density difference (g/cm^3)	$k_1 = V_{c,o}{}^{1/2}$ (cm/s)	k_2	Reference
0.6	Benzene-water	0.725	1.0	0.12	9.07	0.834	Dell and Pratt
1.0	Benzene-water	0.785	1.0	0.12	11.28	1.048	Dell and Pratt
1.0	Benzene-water	0.795	1.0	0.12	11.70	1.077	Dell and Pratt
0.635	Benzene-water	0.745	1.0	0.12	9.32	0.857	Dell and Pratt
0.453	Benzene-water	0.674	1.0	0.12	9.10	0.837	Dell and Pratt
1.27	Methylisobutyl ketone-water	0.748	1.0	0.195	17.16	1.579	Dell and Pratt
1.27	Dibutylcarbitol-water	0.618	1.0	0.113	13.60	1.251	Dell and Pratt
1.0	Dibutylcarbitol-water	0.797	1.0	0.113	11.26	1.036	Dell and Pratt
1.0	Dibutylcarbitol-water	0.787	1.0	0.113	10.75	0.989	Dell and Pratt
0.635	Dibutylcarbitol-water	0.745	1.0	0.113	9.32	0.858	Dell and Pratt
0.600	*i*-octane-water	0.725	1.0	0.308	12.29	1.131	Dell and Pratt
1.0	*i*-octane-water	0.8	1.0	0.308	13.93	1.282	Dell and Pratt
1.0	Butylacetate-water	0.79	1.0	0.117	11.69	1.076	Dell and Pratt
1.0	Butylacetate-glycerol solution	0.79	1.65	0.157	11.37	1.046	Dell and Pratt
1.0	Butylacetate-glycerol solution	0.79	2.32	0.184	12.88	1.185	Dell and Pratt
1.0	Butylacetate-glycerol solution	0.79	5.7	0.237	13.50	1.242	Dell and Pratt
1.0	Chlorex-water	0.795	1.0	0.22	14.40	1.325	Dell and Pratt
1.0	Chlorex-water	0.795	1.0	0.22	14.69	1.352	Dell and Pratt
1.0	Chlorex-water	0.795	1.0	0.22	14.00	1.288	Dell and Pratt
1.0	Chlorex-water	0.793	1.0	0.22	14.13	1.300	Dell and Pratt
1.0	CCl$_4$-water	0.798	1.0	0.6	17.36	1.597	Dell and Pratt
1.905	Benzene-water	0.755	1.0	0.12	19.87	1.830	Dell and Pratt
2.5	Benzene-water	0.777	1.0	0.12	25.71	2.370	Dell and Pratt
2.5	Dibutylcarbitol-water	0.753	1.0	0.114	12.55	1.150	Dell and Pratt
1.905	Methylisobutyl ketone-water	0.753	1.0	0.195	21.65	1.992	Dell and Pratt
1.27	Methylisobutyl ketone-water	0.725	1.0	0.195	21.18	1.949	Dell and Pratt
0.635	Gasoline-water	0.534	1.0	0.16	8.67	0.798	Breckenfeld and Wilke
0.635	Gasoline-water	0.534	1.0	0.16	8.16	0.751	Breckenfeld and Wilke
0.635	Gasoline-water	0.534	1.0	0.2	8.78	0.808	Breckenfeld and Wilke
0.635	Gasoline-water	0.534	1.0	0.2	9.0	0.828	Breckenfeld and Wilke
0.635	Methylisobutyl ketone-water	0.534	1.0	0.2	10.04	0.924	Breckenfeld and Wilke
0.635	Toluene-glycerol solution	0.534	2.77	0.23	7.94	0.731	Breckenfeld and Wilke
1.27	Naphtha-water	0.74	0.98	0.15	12.91	1.188	Breckenfeld and Wilke
1.27	Naphtha-water	0.74	0.98	0.15	13.53	1.245	Breckenfeld and Wilke
1.27	Gasoline-water	0.707	0.88	0.215	14.24	1.310	Crawford and Wilke
3.81	Gasoline-water	0.679	0.88	0.215	19.25	1.771	Crawford and Wilke
2.54	Gasoline-water	0.74	0.88	0.215	19.66	1.809	Crawford and Wilke
2.54	CCl$_4$-water	0.728	0.44	0.58	25.10	2.310	Crawford and Wilke
2.54	CCl$_4$-glycerol solution	0.722	0.41	0.44	23.79	2.190	Crawford and Wilke
0.635	Bismuth-molten salt	0.84	12.0	6.28	15.87	1.460	Hannaford et al.
0.635	Woods metal-water	0.94	0.33	8.67	32.8	3.020	Johnson et al.
0.635	Toluene-water	0.559	0.894	0.117	7.79	0.717	Ballard and Piret
0.635	Toluene-water	0.559	0.894	0.117	7.59	0.698	Ballard and Piret
0.635	Petroleum-ether-water	0.559	0.894	0.26	7.15	0.668	Ballard and Piret
0.635	CCl$_4$-water	0.559	0.894	0.543	10.42	0.959	Ballard and Piret
1.27	Petroleum ether and CCl$_4$-water	0.603	0.894	0.154	13.07	1.202	Ballard and Piret
1.27	Petroleum ether and CCl$_4$-water	0.603	0.894	0.55	23.16	2.131	Ballard and Piret
1.27	Petroleum ether and CCl$_4$-water	0.603	0.894	0.4	20.45	1.882	Ballard and Piret
1.27	Petroleum ether and CCl$_4$-water	0.603	0.894	0.2	14.32	1.318	Ballard and Piret
1.27	Petroleum ether and CCl$_4$-water	0.603	0.894	0.11	10.32	0.950	Ballard and Piret
1.27	Petroleum ether and CCl$_4$-water	0.603	0.894	0.26	16.71	1.537	Ballard and Piret
0.953	CH$_2$Br$_2$-water	0.595	1.0	1.485	27.5	2.53	This study
0.953	CCl$_4$-water	0.595	1.0	0.60	19.5	1.79	This study
0.953	Hg-glycerol solution	0.656	15.0	12.4	29	2.67	This study
0.953	Hg-water	0.656	1.0	12.5	35	3.22	This study
0.953	Hg-water	0.757	1.0	12.5	31	2.85	This study

$$F = \frac{\Sigma(y - y_{\text{mean}})^2/(n_{\text{coefficients}} - 1)}{\Sigma(y - y_{\text{predicted}})^2/(n_{\text{data}} - n_{\text{coefficient}})}$$

A higher F ratio indicates a better correlation. The F ratio was found to be increased (or the correlation improved) by eliminating interfacial tension as a variable from both correlations and by removing μ_c from the $V_{d,o}{}^{1/2}$ correlation.

Previous authors (Breckenfeld and Wilke, 1950; Crawford and Wilke, 1951; Ballard and Piret, 1950; and Dell and Pratt, 1951) have used the external surface area per unit volume of packing as a parameter and attempted to correlate data from different packing shapes (Raschig rings, Berl saddles, etc.). In most gas-liquid systems, the packing is wet by the dispersed liquid phase, and the contact area between the two phases is approximately equal to the

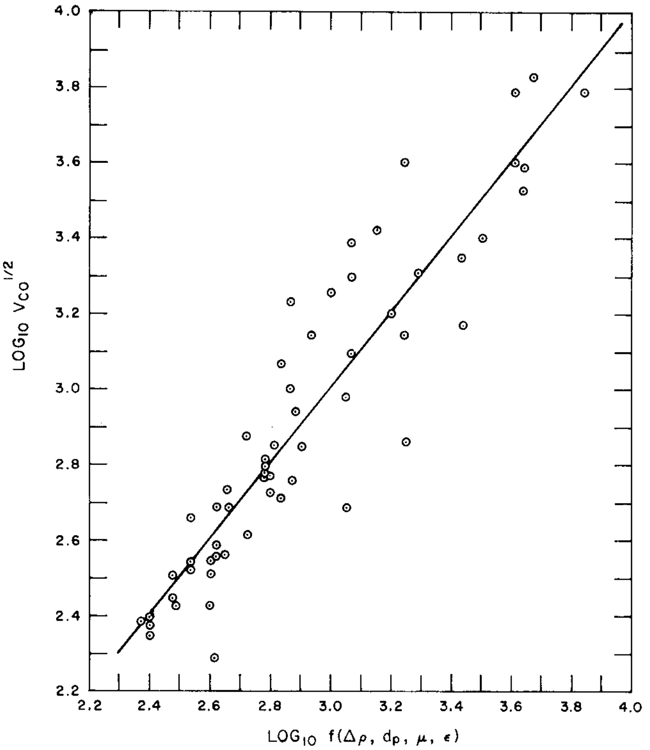

Fig. 3. Comparison of measured and predicted values at $V_{c,o}^{1/2}$.

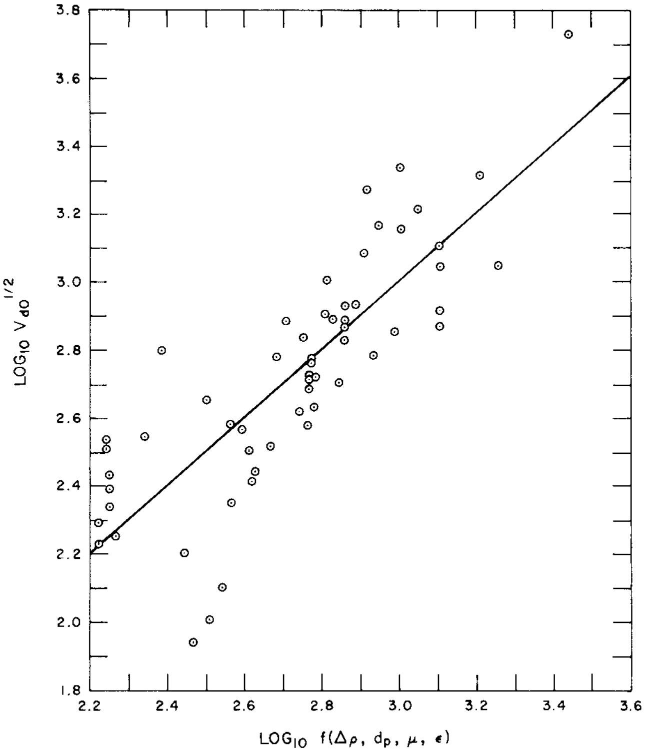

Fig. 4. Comparison of measured and predicted values of $V_{d,o}^{1/2}$.

packing area. In such instances, there is a theoretical basis for using this parameter and for including different packing shapes in a single correlation. In liquid-liquid systems, operating with packing that is not wet by the dispersed phase, the dispersed phase forms small droplets; the interfacial area is then equal to the surface area of the droplets and not that of the packing. Hence it is unlikely that packing area can be used to relate data from several packing shapes with a single flooding correlation.

The best correlations found for the data in Table 1 were

$$V_{c,o}^{1/2} = (23.8 \pm 0.6)\Delta\rho^{0.269 \pm 0.015}\, d_p^{0.494 \pm 0.046}\, \mu_c^{-0.084 \pm 0.030}\, \epsilon^{0.50} \quad (2)$$

$$V_{d,o}^{1/2} = (28.2 \pm 2.1)\Delta\rho^{0.124 \pm 0.017}\, d_p^{0.196 \pm 0.062}\, \epsilon^{1.28 \pm 0.18} \quad (3)$$

The ranges shown in these equations correspond to ± one standard error. As seen, no standard deviation is given for the exponent of ϵ in Equation (2). When Raschig ring data alone are used, the range of void fraction values available is limited, and the data are not well distributed over that range. The first regression suggested that the exponent for the void fraction should be 0.35 ± 0.15. Fixing the exponent at 0.5, however, gave an even higher F ratio. (The variance decreased by more than 20%.) Exploratory regressions with fixed exponents of 0.45 and 0.55 yielded lower F ratios, suggesting a minimum sum of residual squares for values of this exponent near 0.50. The F factors for these correlations were 60 and 35, respectively. The latter values indicate a high degree of confidence that the correlation is valid (greater than 99%); the scatter in predicted and measured results is significant but not unreasonable for flooding data. The scatter around the correlation is illustrated in Figures 3 and 4, where the common logarithm of the predicted parameters is plotted as a function of the common logarithm of the measured value.

Equations (2) and (3) can be combined into a single expression in the form of Equation (1) as follows:

$$V_{c,o}^{1/2} + (0.844\Delta\rho^{0.145}\, d_p^{0.298}\, \mu_c^{-0.084}\, \epsilon^{-0.078})V_{d,o}^{1/2} = 23.8\Delta\rho^{0.269}\, d_p^{0.494}\, \mu_c^{-0.084}\, \epsilon^{0.5} \quad (4)$$

Equation (4) is believed to be a significant improvement over previous correlations since it is based on data covering a wider range of physical properties than correlations developed thus far. The utility of the present correlation will be most significant for systems comprised of fluids with a high density difference. The equation, however, is not dimensionless, and care must be taken to use the correct units.

DISCUSSION OF FLOODING RESULTS

Comparison of Present Correlation with Previous Correlations

The fit of Equation (4) to the data in Table 1 is compared with that of three previous correlations in Table 2. These correlations also predict straight lines on square-root plots such as Figure 1 and can be arranged into the same form as Equation (4). A convenient way to compare the correlations is to compare predicted intercepts, $V_{c,o}^{1/2}$ and $V_{d,o}^{1/2}$, with each other and with the least-squares fits to each data set.

Since the data used for this comparison are also those used to develop the new correlation, one should expect the new correlation to be as good as or better than previous correlations. The interesting question, however, is whether this difference is important. In other words, has the new correlation significantly improved our ability to predict flooding rates?

We are also interested in comparing the correlations with low-density data. The information given in Table 1 is divided into two regions: conventional low-density data ($\Delta\rho < 0.5$) and high-density data ($\Delta\rho > 0.5$). Table 2 gives comparison of the correlations for data from each of these regions, along with a comparison for all the data. For each intercept datum point listed in Table 1, the fractional error e_f of each correlation was evaluated:

TABLE 2. COMPARISON OF THE PROPOSED FLOODING RATE CORRELATION AND PREVIOUS CORRELATIONS WITH THE EXPERIMENTAL DATA

	All data		Low $\Delta\rho$, $\Delta\rho < 0.5$ g/cm^3		High $\Delta\rho$, $\Delta\rho > 0.5$ g/cm^3	
Investigators	$\Delta V_{c,o}{}^{1/2}$	$\Delta V_{d,o}{}^{1/2}$	$\Delta V_{c,o}{}^{1/2}$	$\Delta V_{d,o}{}^{1/2}$	$\Delta V_{c,o}{}^{1/2}$	$\Delta V_{d,o}{}^{1/2}$
Watson and McNeese, (this study)	0.276	0.209	0.293	0.213	0.204	0.203
Breckenfeld and Wilke	0.825	0.829	0.842	0.857	0.795	0.746
Crawford and Wilke	0.903	0.904	0.926	0.935	0.847	0.811
Dell and Pratt	0.324	0.628	0.309	0.574	0.394	0.844

$$e_f = \frac{V_{\text{calc}}{}^{1/2} - V_{\text{meas}}{}^{1/2}}{V_{\text{meas}}{}^{1/2}}$$

The overall fractional error, defined as

$$\Delta V_{c,o}{}^{1/2}, \Delta V_{d,o}{}^{1/2} = \sqrt{\frac{\Sigma e_f^2}{n-1}} \qquad (5)$$

is tabulated in Table 2 for each correlation and both intercepts (denoted by $\Delta V_{c,o}{}^{1/2}$ and $\Delta V_{d,o}{}^{1/2}$). The fractional error is defined in such a manner that it resembles a standard deviation. Thus, the lower the value reported in Table 2, the better the correlation.

Note that after tests with both high- and low-density data, Equation (4) is found to be significantly more accurate than any of the other correlations shown in Table 2. The fractional errors in $V_{c,o}{}^{1/2}$ and $V_{d,o}{}^{1/2}$ range from 0.20 to 0.30. The correlation of Dell and Pratt is considered to be the most accurate of the previous correlations; yet, even it gives significantly larger fractional errors than does Equation (4). For example, while the error is 0.30 to 0.40 at the $V_{c,o}{}^{1/2}$ intercept, the accuracy diminishes further at higher V_d values. Both of the other correlations tested are considerably less accurate; their fractional errors range from approximately 0.80 to 0.90.

Differences between Equation (4) and the previous correlations can be further illustrated by comparing the dependence of flooding rates on several parameters, that is, by comparing the exponents of these parameters in the various correlations. The exponent for $\Delta\rho$ is approximately unity in correlations proposed by Breckenfeld and Wilke (1950) and Crawford and Wilke (1951), while it is near 0.5 in correlations proposed by Ballard and Piret (1950) and by Dell and Pratt (1951). The latter value is in agreement with Equation (4). The exponent for the specific packing area a is near -0.5 for the correlations of Ballard and Piret and of Dell and Pratt and for the high Reynolds number correlation of Crawford and Wilke. On the other hand, the exponent is near -1 for the correlation of Breckenfeld and Wilke and for the low Reynolds number correlation of Crawford and Wilke. Since the specific packing area is approximately inversely proportional to the packing diameter, the -1 value agrees with Equation (4). Similar differences exist in the exponents of μ_c and ϵ. Under many conditions, these differences can be quite important, and extrapolation of the earlier correlations can result in widely different predictions. Equation (4), however, was developed from data covering a much wider range of physical properties than the previous correlations, and it should prove to be more reliable in predicting flooding rates with fluids over a broad range of densities or in extrapolating data obtained with packing materials other than Raschig rings.

Interpretation of Flooding Results

Because flooding is a complex phenomenon, perhaps one should expect to develop only an empirical correlation such as Equation (4) at this time. However, an attempt was made to rationalize or interpret the results in Equations (2), (3), and (4) from qualitative knowledge of countercurrent flow patterns in packed columns. At high continuous phase and low dispersed phase flow rates, the dispersed phase moves up or down the column in the form of small droplets. The dependence of flooding rates on density difference and void fraction is essentially that which would be expected from the settling rates of separate spheres. In the inertial region, spheres settle with an approximately constant drag coefficient; therefore, the settling (slip) velocity should be proportional to the square root of the density difference. In Equation (4), the dependence (0.538) is near 0.5. Furthermore, in the inertial region, flooding rates should not be a strong function of continuous phase viscosity; that is, power dependence on viscosity should be considerably less than unity. The dependence as shown in Equation (4) is significant but small (0.168), which is not inconsistent with the physical model just described.

At high dispersed phase flow rates, the droplets coalesce into larger droplets, which fill some of the packing openings. It is more difficult to rationalize the dependence of $V_{d,o}$ on the significant parameters with physical interpretations. In this range of flow rates, interaction of the dispersed phase with the packing is increased; thus, the viscosity of the continuous phase should have a decreased effect. This proved to be true; the correlation was improved by eliminating μ_c as a parameter. Flooding rates show weak dependence on packing diameter but a strong dependence on void fraction. This latter term does not vary over a wide range in the case of Raschig rings; nevertheless, it is statistically significant.

HOLDUP

The authors previously reported that a single parameter, the superficial slip velocity, could be used to describe both holdup of the dispersed phase and flooding rates in a mercury-water system. New data from the current study indicate that the superficial slip velocity is essentially independent of the flow rate in other high-density systems (for example, mercury-glycerol). We have just shown, however, that flooding rates do not correspond to constant slip velocity. Thus, it appears that the flow patterns are somewhat different at conditions well below flooding and at conditions very near flooding. In the former case, the dispersed phase is in the form of small droplets, while these droplets tend to coalesce near flooding. This is especially evident at high dispersed phase flow rates.

Data obtained with lower-density fluids also suggest that holdup can be approximately described by a constant slip velocity. Previously, Gayler, Roberts, and Pratt (1953) presented results showing that, with conventional low-density fluids and very low values of holdup (< 10%), another characteristic velocity

$$V_o = \frac{V_s}{1 - X} \tag{6}$$

is more nearly constant than V_s. Examination of the present holdup data, data of Gayler, Roberts, and Pratt (1953), and data from an earlier study of Gayler and Pratt (1951) reveals that neither V_s nor V_o is a satisfactory parameter for correlating holdup over a wide range of fluid properties and flow rates. Both our data and that of Gayler and Pratt (1951) contained primarily high values of holdup ($>$ 10%), and in such cases V_s appears to be the preferred correlating parameter. This is illustrated in Figure 2 of Watson and McNeese (1973). The data of Gayler, Roberts, and Pratt (1953) contained lower values of holdup (most values were $<$ 10%), and V_o was shown to be more nearly constant. At low values of holdup, there is little difference between V_o and V_s. Generally, V_s is believed to be a more useful correlating parameter over a wide range of holdup values. However, neither of the parameters is as accurate as one may desire, and improved correlations, especially those with a theoretical basis, are needed.

ACKNOWLEDGMENT

This work was sponsored by the U.S. Atomic Energy Commission under contract with Union Carbide Corporation. The authors would like to express their appreciation to John S. Taylor, R. O. Payne, and several students and Directors of the Massachusetts Institute of Technology Chemical Engineering Practice School who made most of the measurements and otherwise assisted in the study.

NOTATION

a = cm² of packing surface/cm³ of packing volume
d_p = diameter of packing, cm
V_c = superficial velocity of the continuous phase, cm/s
V_d = superficial velocity of the dispersed phase, cm/s
$V_{c,f}$ = superficial continuous phase velocity at flooding, cm/s
$V_{d,f}$ = superficial dispersed phase velocity at flooding, cm/s
V_o = characteristic velocity defined by Equation (6), cm/s
V_s = superficial slip velocity, cm/s

Greek Letters

$\Delta\rho$ = difference in densities of dispersed and continuous phases, g/cm³
ϵ = void fraction of the packing, dimensionless
μ = viscosity, poise
$\Delta V_{c,o}{}^{1/2}$ = defined by Equation (5)
$\Delta V_{d,o}{}^{1/2}$ = defined by Equation (5)

Subscripts

c, d = continuous and dispersed phases, respectively
o = intercept value; flow rate of other phase approaching zero

LITERATURE CITED

Ballard, J. H., and E. L. Piret, "Limiting Flow Phenomena in Packed Liquid-Liquid Extraction Columns," *Ind. Eng. Chem.*, **42**, 1088 (1950).

Breckenfeld, R. R., and C. R. Wilke, "Limited Flows in Packed Extraction Columns," *Chem. Eng. Progr.*, **46**, 187 (1950).

Crawford, J. W., and C. R. Wilke, "Limited Flows in Packed Extraction Column; Correlations for Larger Packing," *ibid.*, **47**, 423 (1951).

Dell, F. R., and H. R. C. Pratt, "Liquid-Liquid Extraction, Part I. Flooding Rates for Packed Columns," *Trans. Inst. Chem. Engrs.*, **29**, 39 (1951).

Gayler, R., and H. R. C. Pratt, "Liquid-Liquid Extraction, Part II. Holdup and Pressure Drop in Packed Columns," *ibid.*, p. 110.

Gayler, R., N. W. Roberts, and H. R. C. Pratt, "Liquid-Liquid Extraction, Part IV: A Further Study of Hold-up in Packed Columns," *ibid.*, **31**, 57 (1953).

Hannaford, B. A., J. S. Watson, C. W. Kee, and H. D. Cochran, Jr., "Hydrodynamics and Mass Transfer in Packed Columns," paper presented at the National Meeting of AIChE, St. Louis, Mo. (1972).

Johnson, T. R., R. D. Pierce, F. G. Tents, and E. F. Johnson, "Behavior of Countercurrent Liquid-Liquid Columns with a Liquid Metal," *AIChE J.*, **17**, 14 (1971).

Watson, J. S., and L. E. McNeese, "Holdup, Flooding, and Pressure Drop in Packed Columns During Countercurrent Flow of Mercury and Water," *ibid.*, **19**, 230 (1973).

Manuscript received February 11, 1975; revision received May 11, and accepted June 9, 1975.

Group-Contribution Estimation of Activity Coefficients in Nonideal Liquid Mixtures

A group-contribution method is presented for the prediction of activity coefficients in nonelectrolyte liquid mixtures. The method combines the solution-of-functional-groups concept with a model for activity coefficients based on an extension of the quasi chemical theory of liquid mixtures (UNIQUAC). The resulting UNIFAC model (*UNI*QUAC *F*unctional-group *A*ctivity *C*oefficients) contains two adjustable parameters per pair of functional groups.

By using group-interaction parameters obtained from data reduction, activity coefficients in a large number of binary and multicomponent mixtures may be predicted, often with good accuracy. This is demonstrated for mixtures containing water, hydrocarbons, alcohols, chlorides, nitriles, ketones, amines, and other organic fluids in the temperature range 275° to 400°K.

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