BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 51 (11), 3381—3382 (1978)

Mass-transfer Experiment through the Water–Benzene Interface in a Capillary Tube

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(Received February 17, 1978)

Synopsis. In order to confirm a previous discussion of a mass-transfer experiment that indicated a high interfacial resistance, an experiment using a capillary tube was done for the transfer process of butylamine through the water–benzene interface at 50 °C. The results obtained agree with the preceding ones.

In a preceding paper,1) it was described that the resistance ($\Delta F^{*}_{d2}=18$ kcal/mol, 50 °C) against which propylamine and butylamine molecules were transferred through the water–benzene interface agreed well with the results of another study2) about the transfer rates of fatty acids through liquid-liquid interfaces. However, the experiment described in the preceding paper showed confused results that the diffusion coefficients measured with the same apparatus as in the transfer experiment were much larger than the values estimated from the literature, and that their concentration dependences could not be disregarded; the author ascribed this discrepancy to the large sectional-area of mass transfer and to the existence of a gas-liquid interface.

In the present paper, the results and its subsequent analysis of an experiment done in order to confirm the discussion in the preceding paper, are described for the transfer process of butylamine through the water–benzene interface at 50 °C, using a capillary tube so as to get diffusion coefficients nearly equal to the literature values.

Experimental and Results

The mass-transfer cell used is a U-shaped glass-tube on the whole, one arm of which has a 1.5 mm (ID) capillary with three Teflon cocks—at both ends and at the middle point; the part from the middle cock to the upper end is called the first capillary, which is to be filled with a benzene solution, while the lower half is called the second capillary, which is to be filled with water. The second capillary is equipped with an array of six pairs of platinum electrodes for determination of electric conductivity.

In order to obtain the temperature constancy and electric insulation of the leading wires, the cell is set in a cylindrical glass-container filled with chemically pure xylene, and then the whole is set in a thermostat.

Opening the middle cock of the cell causes the transfer of the solute (butylamine) from the first phase (benzene) to the second (water). The electrode circuits are automatically switched on and off in turn, and the conductivities are recorded.

In the case of the measurement of the diffusion coefficients in water, aqueous solutions were used instead of benzene solutions, but in the same manner. The electrode sensitivity (equivalent to the cell constant) for each pair of electrodes was referred to the conductivity for an 0.02 M aqueous solution of potassium chloride.

As a result of the transfer experiments, the time dependences of the conductivity of each pair of electrodes were obtained, and were then translated to the concentration changes. The concentration distributions in the second phase at various times were obtained by the interpolation of the concentration changes, and the fitting curves of the concentration distributions were obtained by means of the least squares; the amounts of transfer at the assigned times were obtained by the integration of the fitting curves.

In the measurement of the diffusion coefficients of butylamine in water at 30 and 50 °C, both values calculated from the time dependence of the concentration at the pair of electrodes nearest to the water–benzene interface and calculated from the change in the amount of transfer agreed well with that estimated by Wilke's method3) from the literature; the diffusion coefficients in benzene were not measured because of the difficulty of determining them. In the calculation of the interfacial resistance, the diffusion coefficients estimated from the literature were used (D_1 (in benzene)$=3.21\times10^{-5}$, D_2 (in water)$=1.79\times10^{-5}$ cm^2/s).

Two points of special attention were found in this experiment. (1) When the initial concentration in the first phase was sufficiently high, the analysis became difficult, because the change in concentration tended to be complicated; this means that a turbulence, presumably caused by the Marangoni effect,4) occurred and continued for a long time. Consequently, it was necessary to select an initial concentration low enough so as to get a normal pattern of the concentration change ($c_{10}<0.01$ M). (2) When the electrode sensitivities that had been determined in advance were used for obtaining the transfer amount after a long time (about 20 days), unreasonably large values5) were obtained; this may signify that the electrode sensitivity gradually increased in this experiment. Nevertheless, a relative comparison of the transfer amounts after a long time is considered to be feasible,6) because the variation in the electrode sensitivity may become negligible after a certain time.

The results of determination are indicated in Table 1. Here, suffixes a and b have the following meanings. When the transfer amount was computed by integration from the concentration-distribution observed, $c=a_1+a_2x+a_3x^2$ in (a) and $c=a_1+a_2x+a_3x^2+a_4x^3$ in (b) were used for the functional mode of concentration (c: concentration; x: distance from the interface; a_i:

Table 1. Results of determination

Sample	l [cm]	$c_{10}\times 10^{6}$ [mol/cm^3]	$t_1\times 10^{-6}$ [s]	$t_2\times 10^{-6}$ [s]	$t_3\times 10^{-6}$ [s]	q_1/q_3	q_2/q_3
1a	8.48	8.22	0.968	1.200	1.500	0.813	0.911
1b	8.48	8.22	1.000	1.200	1.400	0.837	0.927
2a	10.35	5.00	0.900	1.200	1.400	0.904	0.969
2b	10.35	5.00	1.000	1.200	1.400	0.926	0.969

Table 2. Results of calculation

Sample	$k_{d2}\times 10^{9}$[mol/cm^2 s]	$c'_{20}\times 10^{7}$[mol/cm^3]
1a	1.4	1.3
1b	0.7	0.8
2a	1.9	5.5
2b	1.0	5.7

parameters); l: depth of both phases; c_{10}: initial concentration of solute in the first phase; t_1, t_2, and t_3: contact times; q_1, q_2, and q_3: transfer amount of the solute at t_1, t_2, and t_3 respectively (mol/cm^2).

Estimation of the Interfacial Resistance

Assigning an arbitrary value to q_1 (or q_3) on the condition that q_1/q_3=const. determines a pair of values, q_1 and q_3, and enables one to compute the desorption rateconstant (k_{d2}) of the solute from the interface to the second phase and the average concentration (c'_{20}) in the second phase immediately after the cessation of an abnormally rapid process, if any, after the procedure described in the preceding paper. The computation was repeatedly made on varied values of q_1 so as to get Curve A on the k_{d2}-c'_{20} plane; Curve B was obtained in the same manner on the condition that q_2/q_3= constant.

As may be seen from drawing Curve A and Curve B from a theoretical change in the transfer amount on definite conditions, Curve A is a tangent which touches Curve B at a point representing the k_{d2} and c'_{20} given as the conditions. We take the k_{d2} sought to be at the minimum point of the difference, c'_{20}(B)-c'_{20}(A), where c'_{20}(A) and c'_{20}(B) are the values of c'_{20} on Curve A and Curve B respectively, corresponding to an assigned value of k_{d2}; the c'_{20} sought is also taken to be the average of c'_{20}(A) and c'_{20}(B) corresponding to the obtained k_{d2}.

The results of calculation are shown in Table 2.

Strictly speaking, the k_{d2} should be obtained by extrapolating the value to $c_{10}=0$,[1] but the values obtained above may be nearly equal to the extrapolated value, because the values of c_{10} are quite small in Table 1. We take the activation free energy of desorption from the interface to the second phase to be ΔF^{*}_{d2}=18.6 kcal/mol, converting the average value of k_{d2} in Table 2, 1.2×10^{-9} mol/cm^2 s;[7] this agrees with the result in the preceding paper.

The author is indebted to Professors Hikoji Inazumi and Tadao Shiba of this Institute for their helpful discussions concerning this subject.

References

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3) C. R. Wilke, *Chem. Eng. Progr.*, **45**, 218 (1949).

4) C. V. Strenling and L. E. Scriven, *AIChE J.*, **5**, 514 (1959).

5) For example, a value larger than the amount of solute in the transfer equilibrium.

6) According to the graph used for obtaining the concentrations from the conductivities, the ratio of concentrations on a curve of a constant electrode sensitivity, corresponding to the fixed conductivities, has a change of only about 5% when the concentration that corresponds to a fixed conductivity has been changed + 100%.

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