Heat Effects in Partially Miscible Liquid Systems

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The heat effects produced by the contacting of two partially miscible liquids can be responsible for the generation of interfacial activity. Austin et al. (1966) noted strong interfacial activity in several partially miscible binary systems and suggested that this was triggered by thermal effects. These thermal effects can become very important, since interfacial activity is considered to be responsible for the enhancement of mass transfer rates as compared to those obtained by pure diffusion.

Davies and Thornton (1977) studied the mass transfer in the furfural/water system between a pendant droplet and the surrounding continuous phase using a Mach-Zehnder laser interferometer. They suggested that microconvection currents were generated due to the large heats of solution, which in turn would be responsible for the large mass transfer rates observed. In a more recent work, Thornton and Anderson (1981) experimentally measured the frequency of disturbances at a predetermined position on the surface of a growing pendant droplet immersed in a second immiscible liquid phase. They found that, when an undistributed solute was present in the continuous phase, a series of violent and sporadic interfacial disturbances took place in the drop. These disturbances were possibly induced by Marangoni effects, which would also be responsible for increased mass transfer rates.

In a study of simultaneous mass and heat transfer in partially miscible liquid-liquid systems, Aguirre (1982a) experimentally measured the temperature changes produced when the two pure liquids are contacted at a planar interface. These measurements were performed in a cylindrical Teflon transfer cell, which was instrumented with six microthermocouples in its axial direction. Five of these thermocouples were placed in the bottom phase, located at distances from the interface ranging between 0.00066 and 0.016 m. The transfer cell was divided in two parts. Each section contained one of the liquids, with the heavier one in the bottom. The two phases were contacted by slowly and smoothly rotating the upper half of the transfer cell. Details concerning the experimental equipment and procedure are reported elsewhere (Aguirre, 1982a; Aguirre et al., 1982b).

In general, the temperature decreased after the contacting of the phases, which was due to the endothermic nature of the mass transfer process. Considering that the behavior at the interface is of more interest for the analysis, the temperature changes at such position were calculated by extrapolation of the experimental data in the bottom phase. Several methods of extrapolation were tried, such as linear, quadratic and cubic spline techniques. All of these methods gave essentially the same results, reason for which linear extrapolation was used. Figure 1 for the nitroethane/2,2,4-trimethylpentane system shows that the interfacial temperature *decreases* very fast after the contacting of the phases takes place. It soon reaches a minimum, followed by an increase in temperature until a relatively steady state value is achieved. This behavior is qualitatively the same for all the partially miscible systems studied, with the exception of one system (water/isobutanol) which showed no significant temperature changes.

Several parameters were defined for each system studied (Aguirre et al., 1982b). Two of these parameters, the maximum interfacial temperature difference $(-\Delta T)_{\max}$ and the time at which this value is obtained ($t_{\max}$), are indicated in Figure 1.

EMPIRICAL CORRELATION

The values of $(-\Delta T)_{\max}$ for all the systems studied were analyzed by trying to correlate them with physical properties of the systems involved. A good choice of physical properties were the heats of solution in both phases since these had to be related to the temperature changes produced. The "maximum theoretical temperature change" for 1 mol of mixture proved to be the best representative parameter involving physical properties of the systems. This "maximum theoretical temperature change," which is represented by $\theta_{\max}$, is defined as the net heat of mixing per unit mole of mixture at saturation conditions divided by the average molar heat capacity of the bottom phase at the same conditions. This definition can be better visualized with the following equation.

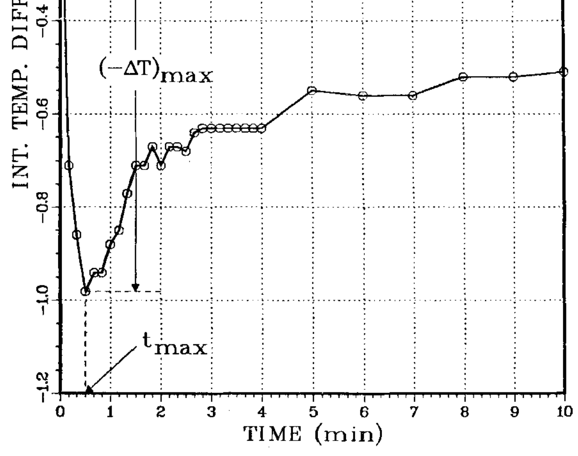

Figure 1. Interfacial temperature difference for nitroethane/2,2,4-trimethylpentane system.

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TABLE 1. EXPERIMENTAL AND PHYSICAL PARAMETERS IN PARTIALLY MISCIBLE SYSTEMS STUDIED

System (j/i)	$(-\Delta T)_{\max}$ [K]	$\theta_{\max}$ [K]	H^{E*}_{ij} [J/mol]	H^{E*}_{ji} [J/mol]
Furfural(F)/Water(W)	0.45	2.04	1,273	25.5
Water(W)/Isobutanol(I)	0.00	0.401	−152	580
Water(W)/Ethyl acetate(EA)	0.30	0.533	−117.8	757.9
Furfural(F)/Cyclohexane(C)	0.62	5.07	1,004.8	669.9
Aniline(A)/Cyclohexane(C)	0.79	7.80	1,517.6	1,381.4
Methanol(M)/n-Hexane(Hx)	0.63	5.11	478	519
Methanol(M)/n-Heptane(Hp)	0.58	4.24	360.1	487.3
Nitroethane(N)/2,2,4-Trimethylpentane(TMP)	0.96	7.70	1,324.0	1,229.6
Acetic anhydride(AA)/ Cyclohexane(C)	0.68	5.68	1,318.8	741.1

The values of the heats of solution at saturation conditions are at 298 K.

$$\theta_{\max} = \frac{\dfrac{H^{E*}_{ij}\rho_j}{(MW)_j} + \dfrac{H^{E*}_{ji}\rho_i}{(MW)_i}}{C_{pmj}\left[\dfrac{\rho_j}{(MW)_j} + \dfrac{\rho_i}{(MW)_i}\right]} \qquad (1)$$

There is an implicit assumption in this equation that the volumes of each phase, which are considered to become rapidly saturated and thus have an important contribution to the net heat of mixing, are equal. In Eq. 1 the subscript i represents the top or lighter phase and the subscript j the bottom or heavier phase. The densities ρ_i and ρ_j are those for each phase at saturation conditions and are calculated by averaging the specific volumes of each pure liquid with the weight fractions at such condition. For the molecular weights $(MW)_i$ and $(MW)_j$, the averaging is done with the mole fractions at saturation conditions. Finally, C_{pmj} is the average molar heat capacity of the bottom phase, which is calculated by using mole fractions at saturation conditions. The heat capacity in the bottom phase was used considering that the values for $(-\Delta T)_{\max}$ were determined by extrapolation of the experimental data in that phase. All physical properties were evaluated at 298 K since the experimental work was performed at room temperature.

Nine partially miscible liquid systems were considered in the present analysis, Table 1. Table 1 also shows the values of $(-\Delta T)_{\max}$, $\theta_{\max}$ and the heats of solution at saturation conditions for both phases at 298 K.

The variable $\theta_{\max}$, as described by Eq. 1, has been named "maximum theoretical temperature change," since it represents the temperature change that would be observed if 1 mol of mixture composed of equal volumes from each phase is perfectly mixed so that all of it reaches saturation in a very short period of time.

The relationship between the values of $(-\Delta T)_{\max}$ and the "maximum theoretical temperature change" $\theta_{\max}$ is shown in Figure 2, where each experimental data point is accompanied by an abbreviation of the partially miscible system to which it corresponds. The data in Figure 2 show a linear behavior except for the water/isobutanol system which did not show any significant temperature changes. Excluding this binary system, these experimental points have been fitted to the following equation.

$$(-\Delta T)_{\max} = a + b\,\theta_{\max} \qquad (2)$$

where:

$$a = 0.260$$

$$b = 0.0767$$

The correlation coefficient for this fit is 0.920 and the standard error of estimate for $(-\Delta T)_{\max}$ is 0.057 K, which can be considered quite good. It can be noticed that the intercept of this straight line is 0.260 K, which would mean that for a value of $\theta_{\max}$ equal to zero, the value of $(-\Delta T)_{\max}$ would be equal to 0.260 K. By definition this cannot be true, since for a heat of mixing of zero, and hence $\theta_{\max} = 0$, the value for $(-\Delta T)_{\max}$ should also be zero. As a consequence, the empirical correlation found between $(-\Delta T)_{\max}$ and $\theta_{\max}$ can only be valid for values of $\theta_{\max}$ greater than approximately 0.50 and therefore in the region close to zero a discontinuity in the correlation would exist. This is represented by the dash line in Figure 2, although more data would be required in this region to prove this. The results presented here could be very useful because, even though the correlation between $(-\Delta T)_{\max}$ and $\theta_{\max}$ is empirical, it could be used for an initial estimation of the temperature differences that would be produced at an interface if the heats of solution at saturation conditions of both phases were known.

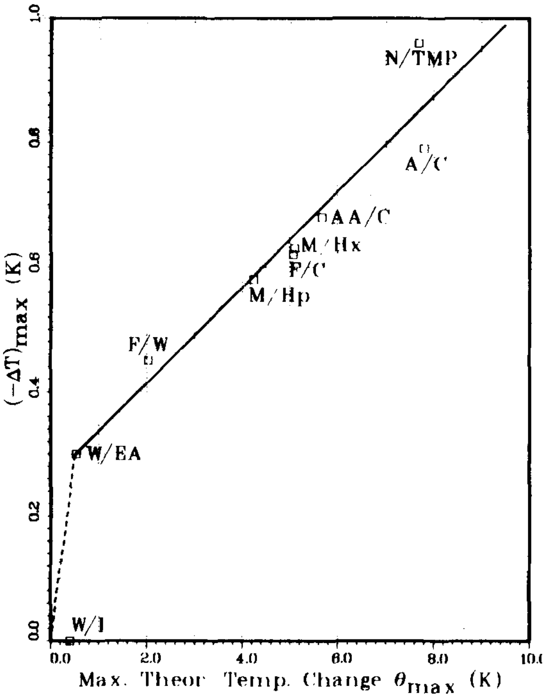

Figure 2. Relationship between $(-\Delta T)_{\max}$ and the maximum theoretical temperature change.

ACKNOWLEDGMENT

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NOTATION

a = adjustable parameter in Eq. 2 (K)
b = adjustable parameter in Eq. 2
C_{pmj} = average molar heat capacity of the bottom phase at saturation conditions and 298 K (kJ/kg·K)

H^{E*} = heat of solution at saturation conditions and 298 K (J/mol)
MW = average molecular weight of liquid phase at saturation conditions (kg/kmol)
$t_{\max}$ = time at which maximum temperature difference occurs (min)
$(-\Delta T)_{\max}$ = maximum experimental temperature difference at the interface (K)

Greek Letters

$\theta_{\max}$ = maximum theoretical temperature change defined by Eq. 1 (K)
ρ = density (kg/m^3)

Subscripts

i = top or lighter liquid phase
j = bottom or heavier liquid phase
ij = physical property for component i in phase rich in component j

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Photochlorination of Methane in a Two-Zone Photoreactor

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In recent studies (Dworkin and Dranoff, 1978; Mazich, 1980; Richard, 1982), the two-zone photoreactor concept was evaluated via the gas-phase photochlorination of chloroform. Lucas (1971, 1973) originally proposed that by-product formation and deposition of opaque films on reactor windows could be eliminated by using a perforated teflon diaphragm or grid to divide the flow reactor into two zones. He suggested that reactive species formed in the photoinitiation zone would flow through the grid into the thermal reaction zone where reaction would be completed.

The previous studies verified that chlorine-free radicals will behave in this way and explored the influence of grid thickness and open area, photoinitiation chamber length and reactant gas flow rates on reactor performance. They showed that increased open area favors higher reaction rates, while increased total gas flow rate or photoinitiation chamber length may increase or decrease reaction rates. The purpose of this study was to investigate the use of the two-zone reactor for the more complex photochlorination of methane.

EXPERIMENTAL

The photochlorinations of methane and its first three chlorine derivatives proceed as:

$$CH_{4-n}Cl_n + Cl_2 \xrightarrow{h\nu} CH_{3-n}Cl_{n+1} + HCl, \quad n = 0, 1, 2, 3 \tag{1}$$

These reactions have been carried out commercially (Hirschkind, 1949; Sconce, 1962), both thermally and photochemically. While thermal chlorination usually requires temperatures in excess of 250°C, photochlorination at 300 to 500 nm will proceed at 25°C. In either case, all four reaction products (CH_3Cl, CH_2Cl_2, $CHCl_3$, and CCl_4) are produced, even at low conversions which should favor the production of CH_3Cl, unless the feed composition is specifically regulated. (For example, a high methane:chlorine ratio favors the production of CH_3Cl.) Furthermore, methane and chlorine form explosive mixtures between approximately 40 and 90 mol % chlorine (Seya, 1970)—another factor in determining reactor feed conditions.

Methane photochlorination was studied most extensively by Ritchie and Winning (1950), who showed that dark reaction was negligible at 25°C and that the reaction proceeded by a radical chain mechanism.

For the production of CH_3Cl:

$$\text{Initiation: } Cl_2 \xrightarrow{h\nu} 2\,Cl\cdot \tag{2a}$$

$$\text{Propagation: } Cl\cdot + CH_4 \rightarrow CH_3\cdot + HCl \tag{2b}$$

$$CH_3\cdot + Cl_2 \rightarrow CH_3Cl + Cl\cdot \tag{2c}$$

$$\text{Termination: } Cl\cdot + Cl\cdot \xrightarrow{\text{wall}} Cl_2 \tag{2d}$$

$$CH_3\cdot + Cl\cdot \xrightarrow{\text{wall}} CH_3Cl \tag{2e}$$

$$CH_3\cdot + CH_3\cdot \xrightarrow{\text{wall}} C_2H_6 \tag{2f}$$