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THERMOPHYSICAL PROPERTIES OF THE UREA–FORMALDEHYDE SYSTEM MEASURED UNDER NEAR-INDUSTRIAL-PROCESS CONDITIONS

K. STARZYNSKA and D. WYRZYKOWSKA-STANKIEWICZ

Research Institute for Industrial Chemistry, 01-793 Warsaw (Poland)

S.L. RANDZIO

Polish Academy of Sciences, Institute of Physical Chemistry, ul. Kasprzaka 44/52,
01-224 Warsaw (Poland)

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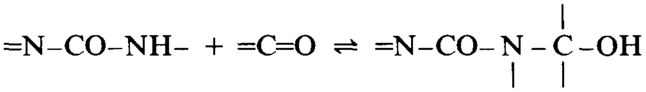
ABSTRACT

The results of calorimetric measurements of the overall heat effects, specific heats, adiabatic temperature courses and thermokinetic data for the urea–formaldehyde reactions are presented. The measurements have been performed under near-industrial-process conditions with respect to temperature, reactant ratio and pH of the reaction medium. In the mildly alkaline pH region, the measurements have been performed in two steps showing the concentration dependence of the enthalpy changes. The resulting reaction mixtures had almost identical specific heats regardless of the initial amount of urea added. The specific heats of concentrated formaldehyde solutions determined at 324 K proved to be quite close (~ 5%) to the ideal mixture C_p estimates.

INTRODUCTION

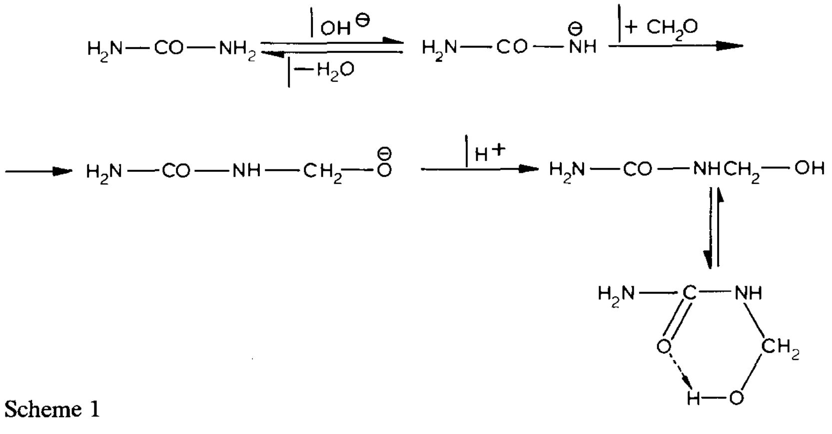
The reaction between a compound carrying NH group (e.g. urea) and a carbonyl compound (e.g. formaldehyde) primarily involves addition



$$=\text{N}-\text{CO}-\text{NH}- + =\text{C}=\text{O} \rightleftharpoons =\text{N}-\text{CO}-\underset{|}{\text{N}}-\overset{|}{\underset{|}{\text{C}}}-\text{OH}$$

The primary reaction step may, or may not, be either acid- or base-catalysed to yield the *N*-methylolurea depicted in Scheme 1.

When carried out in aqueous formaldehyde, the reaction involves unhydrated formaldehyde and the urea anion, which is assumed to be a resonance structure [1]. The resulting *N*-methylolurea is stabilized by an intramolecular hydrogen bond. With a 1 : 1 molar ratio of the reactants, it has been established that the bimolecular reaction yields monomethylolurea exclusively, but with formaldehyde used in an excess of 1 : 2, dimethylolurea



Scheme 1

also forms [2]. The pure mono- and dimethylol derivatives are colourless solids melting at 384 K and 399 K [3], respectively, both fairly soluble in cold water.

Thermochemical data for this system are scarce. The heats of reactions of formation of mono- and dimethylolureas in alkaline solutions have both been determined calorimetrically to be 20.5 kJ mol^{-1} [4]. The activation energies for the primary reaction step and for the hydrolysis of *N*-methylolurea have been evaluated as 64.4 and 85.3 kJ mol^{-1}, respectively [4]. However, these data are insufficient to evaluate the thermochemical and thermokinetic data for the real primary process of formation of urea–formaldehyde resins with all the associated thermal effects, such as dissolution of solid urea in aqueous concentrated formaldehyde, conditioning the solute to the reaction temperature, separation of solid products, etc., when considered together. Thus, it was deemed desirable to measure the overall heat effects, both as energy and power, the heat capacity and the adiabatic temperature course observed in the complex reaction under conditions closely approximating those of a large-scale process.

EXPERIMENTAL

Measurements of power and energy evolved by reactions in alkaline solutions

An all-glass 50 ml reactor was used as a calorimetric vessel. The upper part of the reactor carried an HP-2850 quartz thermometer probe, a calibration resistance heater and a stirrer mounted via a ground-glass joint and driven electrically. The reactor holding a weighed amount of aqueous formaldehyde was closed and placed in a water thermostat controlled by a Unipan type 650 temperature controller [5]. The HP-2850 probe was operated in conjunction with an HP-2804 quartz thermometer, an electronic clock and a printer in order to record the calorimetric temperature changes as a function of time. After the experimental temperature had been attained, a weighed amount of urea at ambient temperature was poured into the reactor and the calorimetric temperature changes were recorded while the reaction was proceeding. The power $q(t)$ and the energy $Q(t)$ delivered by the process in the calorimetric reactor as a function of time were determined with the help of formulas (1) and (2) and a program for an ODRA 1204 computer [6]

$$q(t) = \alpha\left\{\theta(t) + \tau\frac{\mathrm{d}\theta(t)}{\mathrm{d}t}\right\} \tag{1}$$

$$Q(t) = \alpha\left\{\int_{t_0}^{t}\theta(t)\,\mathrm{d}t + \tau\int_{t_0}^{t}\mathrm{d}\theta(t)\right\} \tag{2}$$

where θ (K) is the temperature difference between the recorded temperature of the calorimetric reactor and that of the thermostat, α (W K^{-1}) is the heat exchange coefficient between the calorimetric reactor and the thermostat, and τ (s) is the time constant of the calorimetric reactor. The values of the coefficients were determined by standard procedures [7,8] and assumed to be constant during the course of the experiment.

Measurements of heat of reaction in acid solutions

Measurements in acid solutions were performed at 374 K in a Unipan type 600 calorimeter [9] with a reaction vessel equipped with an internal dosing cylinder, a calibration heater and a hydraulic stirrer [10]. A portion of hydrochloric acid was placed in the internal dosing cylinder and the reaction part of the vessel was filled with the reaction mixture obtained from the alkaline polymerization. After thermalization, hydrochloric acid was injected into the reaction mixture. The mixture was stirred continuously. No measurable heat was detected, the only result being a small endothermic effect at noise level, probably caused by opening the dosing cylinder.

Measurements of specific heats

Measurements of specific heats of aqueous concentrated formaldehyde solutions and of the products of their reactions with urea were performed at 324 K in the Unipan calorimeter [9], using the relaxation method, which measures the time constant of the calorimetric vessel filled with a known amount m_x of the substance under investigation. The time constant τ_x is defined by expression (3)

$$\tau_x = \frac{C_v + m_x c_x}{\alpha} \tag{3}$$

where C_v is the heat capacity of the empty calorimetric vessel and c_x is the specific heat of the substance under investigation. The determination of calorimetric time constants has been adequately described in the literature [7,8]. Both C_v and α were determined from two independent measurements of the time constant using two different amounts of water, for which the specific heat is well known. The relaxation method of determining specific heats is valid providing that there are no significant temperature gradients, convection currents, etc., inside the calorimetric cell, and that the heat exchange coefficient α remains unchanged when the calorimetric cell is filled with different liquids, both for reference and under investigation. In order to try to fulfil these conditions, water was taken as the reference material and the calorimetric cell was filled to the same level in all the measurements. The thermal equilibrium of the calorimetric cell was disturbed by the use of an internal calibration heater [11]. Methanol was used to check the measurements performed in order to verify both the instrument and the method used. The value obtained at 324 K, 2.65 ± 0.05 J g^{-1} K^{-1}, compares well with the literature value of 2.70 ± 0.01 J g^{-1} K^{-1} [12].

RESULTS AND DISCUSSION

The results of measurements of overall heat effects in alkaline solutions together with other experimental details are presented in Table 1. The enthalpy ΔH(urea) represents that portion of the process enthalpy which has to be delivered to warm up the solid urea (initial temperature 294 K) to the temperature of the liquid reaction medium. The Q values represent the energies associated with both the dissolution of the solid urea in the reaction mixture and the bond rupture–formation. Runs IA, II, IIIA, IV, VA and VI were carried out with the amounts of urea specified so as to produce formaldehyde : urea mole ratios $s \cong 5.5:1$. In runs VII and VIII, the amounts of urea were adjusted to achieve the ratios $s \cong 2.1:1$. Runs I, III and V involved two steps. Step A was the one just described with $s \cong 5.5:1$. After completion of step A, a further portion of solid urea (294 K) was added to the reaction mixture (step B) to make the eventual ratio $s \cong 2.1:1$, a value almost identical with that used in the single-step runs, VII and VIII. Runs II and VI were like any other step A run, except that they were not followed by a step B. In run IX, the amount of urea was intentionally low and the data recorded were omitted from the calculation scheme.

The Q values obtained from runs IA, II, IIIA, IV, VA and VI, which are arranged in Table 1 in ascending order of s ratios, can be seen to increase as the reactant mole ratio s is increased. They exceed considerably the values obtained from the B runs (IB, IIIB and VB). For step A, the mean thermal effect evaluated by numerical integration

$$Q_{\text{mean}} = \frac{\int_{s1}^{s2} Q(s)\,\mathrm{d}s}{s2 - s1} \tag{4}$$

TABLE 1

Calorimetric and thermokinetic data on specified methylolation reaction runs

Run No.	Step	Temp. (K)	Conc. aq. CH_2O soln.				$CO(NH_2)_2$			s (mol mol^{-1})	pH	Q (kJ)	ΔH (urea) (kJ)	$\Delta H_r(324.5)$		ΔT_{max}^{adiab} (K)
			CH_2O (wt.%)	MeOH (wt.%)	soln (9)	CH_2O (mol)	(g)	(mol)	(%)[a]					(kJ g^{-1})	(kJ mol^{-1})	
I	A	324.5	48.10	3.10	150.2	2.4061	26.5	0.4413	15	5.4528	8.5	10.865	1.259	0.458	27.476	20.0
I	B	324.5	48.10	3.10	150.2	2.4061	42.1	0.7010	31.4	2.1064	8.0	4.213	2.002	0.148	8.866	13.8
II		324.8	48.44	1.12	150.3	2.4247	26.5	0.4413	15	5.4950	7.9	11.925	1.259	0.498	29.878	21.8
III	A	324.5	49.30	2.50	150.4	2.4694	26.5	0.4413	15	5.5963	8.5	13.515	1.259	0.558	33.482	25.4
III	B	324.6	49.30	2.50	150.4	2.4694	44.1	0.7343	31.9	2.1006	8.2	3.528	2.096	0.128	7.659	5.7
IV		324.7	50.20	1.30	151.2	2.5279	26.7	0.4446	15	5.6859	8.0	14.481	1.269	0.590	35.426	26.0
V	A	324.5	52.09	5.60	150.0	2.6022	26.5	0.4413	15	5.8973	8.2	18.320	1.259	0.739	44.371	34.6
V	B	324.5	52.09	5.60	150.0	2.6022	47.9	0.7976	33.2	2.1005	8.0	5.203	2.276	0.156	9.377	7.6
VI		324.8	48.81	3.25	150.2	2.4416	22.5	0.3747	13	6.5170	8.0	12.825	1.069	0.618	37.085	23.6
VII		324.8	49.44	3.94	150.3	2.4748	71.7	1.1939	32.3	2.0729	8.0	14.340	3.047	0.248	14.865	21.2
VIII		324.2	54.35	6.58	152.5	2.7604	78.0	1.2988	33.8	2.1253	8.1	15.600	3.707	0.248	14.865	21.7
IX		324.5	49.50	1.56	88.8	1.4639	7.6	0.1265	7.9	11.5679	8.0	11.324	0.361	1.538	92.335	

[a] Initial percentage urea content in the reaction mixture.

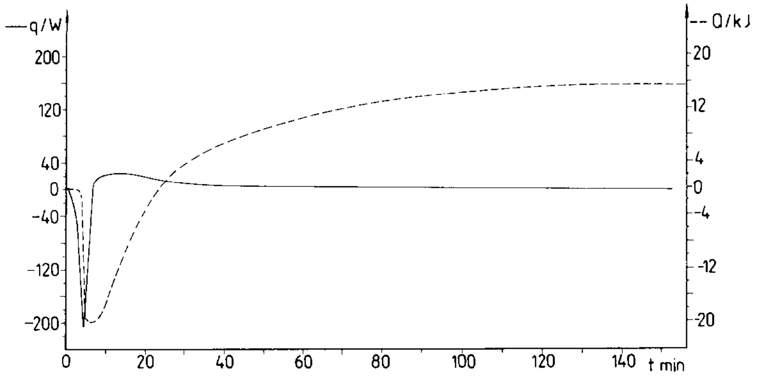


Fig. 1. An example (run VIII) of the heat Q and of the thermal power q delivered by the reaction as a function of time.

from $s1 = 5.45$ to $s2 = 5.90$ is 33.5 ± 0.5 kJ mol^{-1}. For step B, the mean thermal effect calculated by arithmetically averaging the B run (IB, IIIB, VB) Q values is 8.7 ± 0.9 kJ mol^{-1}. The single-step reaction (runs VII and VIII) is accompanied by a net heat effect of 14.86 ± 0.005 kJ mol^{-1}.

An example of the thermokinetic results is presented in Fig. 1, where both the total heat and the thermal power delivered by the reaction as a function of time are shown for run VIII. When dividing the total heat effect by the heat capacity of the respective reaction mixture, one can obtain the maximum temperature increment during the postulated reaction run which would occur regardless of the total amounts of the reactants. The rounded values of $(\Delta T)_{\max}^{\text{adiab}}$ are listed in Table 1 (last column). In a real reactor, temperature increments would be smaller due to heat leakage.

Results of specific heat measurements are listed in Tables 2 and 3. The remarkable consistency of the specific heat values of the aqueous concentrated formaldehyde solutions (Table 2) is worth emphasizing, especially because each specimen was derived from an individual concentration run. A search of the literature has revealed no specific heat data on pure liquid formaldehyde, aqueous formaldehyde methylolureas or solutions thereof. C_p

TABLE 2

Specific heats of concentrated formaldehyde solutions

Concentrated aqueous CH_2O		C_p (J g^{-1} K^{-1})	
CH_2O (wt.%)	MeOH (wt.%)	closed vessel	stirred vessel
48.66	2.38	3.15	
49.00	2.20	3.10	
50.88	1.58	3.09	
50.00	1.38		3.08

TABLE 3

Specific heats of the urea methylolation products

Reactants			Of total CH_2O content				C_p ($J\ g^{-1}\ K^{-1}$)
Urea in formalin (%)	Formalin		CH_2O (%)	$-CH_2OH$ (%)	$-CH_2-O-CH_2$ (%)	$-CH_2-$ (%)	
	CH_2O (%)	CH_3OH (%)					
5	49.00	2.20	79.57	18.53			2.99
10	50.88	1.58	71.80	28.2			3.06
15	50.88	1.58	60.20	39.20			3.12
20	49.00	2.20	54.30	46.00			3.11
25	50.88	1.58	51.40	47.40			2.97
30	49.00	2.20	7.30	84.70	0.36	7.64	3.07

estimates for liquid formaldehyde based on the well-known ideal gas $C_p^{\ominus}$ values for gaseous formaldehyde, when combined additively (ideal case) with the experimental specific heats of water and liquid methanol, gave ideal mixture values for concentrated aqueous formaldehyde solutions which are reasonably consistent (to within around 5%) with the present experimental data (Table 2). The lack of C_p values for methylolureas makes it much more difficult to verify the C_p data obtained for the methylolation product mixture (Table 3). However, the observed C_p values do remain almost constant as the initial urea concentration (i.e. prior to the reaction) is increased. Thus, the partial specific heat of methylolurea is supposed to rise as its concentration is raised. In aqueous urea solutions the partial specific heat of urea has been found to increase as the urea concentration is raised [13], the hydrophobic effect having been suggested as the responsible factor. With methylolureas, the hydrophobic effect is likely to result in a similarly directed tendency. As is evident from Table 3, it is when the initial urea content is above 25% that dimethylolurea begins to form. Thus, all the step A runs, and also runs II, IV and VI, are believed to involve the monomethylolation reaction only, whereas all the step B runs, and also runs VII and VIII, involve the mono- and the dimethylolation reactions together.

From the practical point of view, the presented experimental data, both thermodynamic and thermokinetic, lead to the conclusion that, in the alkaline solution process, the total amount of urea to be added to the formaldehyde solution should be added in a single step. The thermal effect then released and the resulting reactor temperature course will provoke no hazards and the time required for the addition of urea will be kept at a minimum. The three arguments in favour of the single-step addition of urea are: (1) the heat capacity of the reaction mixture remains practically constant as the reaction progresses; (2) at low initial urea concentrations, the reaction heat is considerably greater (run IX); and (3) whether the initial urea concentration is low or high, the thermokinetics and, in particular, the duration of the process are quite similar. For these arguments to be correct, it is necessary to provide for effective mixing in a real reactor.

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