

## TEMPERATURE DEPENDENCE OF DENSITIES AND HEAT CAPACITIES FOR THE METHANOL-UREA SYSTEM

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Data were obtained for the temperature dependences of densities and heat capacities of liquid solutions of the methanol-urea system over the region of their mutual solubility. The temperature region was 298.15 K to 328.15 K.

Experimental dependences of physical properties of the methanol-urea system can be employed in two manners: they can serve for investigation of the real behaviour of this binary system with associating components, where specific interactions of hydrogen bonds are of interest; or — as is the aim of the present work — they provide data requisite for designing syntheses and industrial productions, which are abandoning the initial concept starting from aqueous urea solutions.

### EXPERIMENTAL

#### Preparation and Purity of Substances and Solutions

Methanol of reagent grade was distilled on a 100-plate packed column with stainless steel saddles. The middle fractions were employed; they were stored over 0.3 nm molecular sieves. Chromatographic analysis gave evidence that impurities were present in quantities smaller than 0.01 wt. %. No water could be detected by the Fischer test. Urea was a reagent grade chemical obtained from Carlo-Erba and was used as received.

Solutions for density and heat capacity measurements were prepared by weighing in the substances directly in the pycnometer or in a weighing bottle. During measurements, the solutions were checked analytically by UV spectroscopy. The checking was done to rule out chemical reactions, which might, though to a low extent, occur in the calorimetric vessel which was made of brass; these conceivable reactions include nucleophilic addition of methanol to a carboxy group, or detachment of ammonia associated with the formation of methyl carbamate. Dimethyl carbamate may form in highly dilute urea solutions. The solutions were replaced as many as three times during the measurement. Eight and five urea solutions in methanol were prepared for the density and heat capacity measurements, respectively. The urea mass fraction  $w = 0.1810$  is just below the limit of urea solubility in methanol at 298.15 K.

### Determination of Densities

Densities were measured in 25 cm<sup>3</sup> pycnometers, which had been calibrated with conductivity water over the region of 298.15 K to 308.15 K and with benzene up to 318.15 K. Solutions were prepared by weighing urea in the pycnometer and adding methanol in an amount such that the level of the solution obtained was just below the mark. After mixing and thermostating, one or two drops of pure methanol were added so that the meniscus was at the mark. The thermostat temperature was held constant to within  $\pm 0.005$  K, and the weighing error did not exceed  $1 \cdot 10^{-4}$  g.

### Determination of Heat Capacities

Heat capacities were measured with an adiabatic calorimeter of the static type<sup>1</sup> using the set-up and control unit as described previously<sup>2</sup>. The vessel used for the measurement allowed the heat capacities of the solutions to be determined at the saturated vapour pressure. Thus, a two-phase system of the liquid-vapour type was measured, making it possible to calculate the heat capacity of the solutions on the curve of saturation  $C_s^1$ . The vessel, 10 cm<sup>3</sup> volume, was filled with 9 to 9.5 cm<sup>3</sup> of the solution measured, in dependence on the thermal expansion of the solution and on the temperature region over which the measurement was to be carried out. The vapour space in the calorimetric vessel was small, and no corrections for it had to be made in this work.

The measurement procedure was as described previously<sup>1</sup>. Our experiments carry out in three stages. In the first and third stages, the heat exchange between the calorimetric vessel and its environment was determined before and after the measurement. The second stage served the determination of the heat capacity, which was calculated by means of the relation

$$C_s^1 = [(Q - [Q_z]/\Delta T - C_n)]/m, \quad (1)$$

where  $C_s^1$  is the heat capacity along the saturation curve,  $Q$  is heat supplied to the calorimetric vessel with sample in the second stage of the experiment, and  $\Delta T$  is temperature increase caused by it;  $Q_z$  is correction for the loss flow occurring in the second stage of the experiment, and  $C_n$  is the heat capacity of the empty calorimetric vessel including all measuring, control and design components;  $m$  is the mass of the solution. The heat capacity  $C_n$  was determined by using methanol<sup>3</sup>. The expected error of measurement was 0.3–0.5%.

### RESULTS

The results of measurement of the density of urea solutions in methanol in dependence on temperature and composition are given in Table I. Graphical representation of the results suggested that the density can be expressed as linear functions of temperature and composition:

$$\rho = a_1 + b_1 T [w], \quad (2)$$

$$\rho = a_2 + b_2 w [T], \quad (3)$$

where  $\rho$  is solution density in g/cm<sup>3</sup>,  $a_1$ ,  $b_1$ ,  $a_2$  and  $b_2$  are parameters of the equations,  $w$  is mass fraction, and  $T$  is absolute temperature. The parameters, along with the correlation coefficients, are given in Tables II and III for Eqs (2) and (3), respectively.

The data of the temperature dependences of heat capacities for the methanol-urea solutions are summarized in Table IV. Again, the temperature dependence can be considered linear:

$$C_s^l = a_3 + b_3 T \quad [w]. \quad (4)$$

Parameters of Eq. (4),  $a_3$  and  $b_3$ , for the various compositions are given in Table V along with the correlation coefficient  $r$ .

The data of the temperature dependence of density and heat capacity are consistent with those obtained for the water-urea<sup>4</sup>, water-tetramethylurea<sup>5,6</sup>, and alcohols-tetramethylurea<sup>7</sup> systems. The systems depart appreciably from ideal behaviour,

TABLE I  
Temperature dependences of density (in g/cm<sup>3</sup>) of methanol-urea systems of various composition

w	T, K				
	298.15	303.15	308.15	313.15	318.15
0.0502	0.8072	0.8022	0.7979	0.7932	0.7881
0.0709	0.8155	0.8109	0.8067	0.8018	0.7969
0.0854	0.8221	0.8175	0.8132	0.8084	0.8032
0.1050	0.8306	0.8260	0.8214	0.8165	0.8116
0.1199	0.8365	0.8312	0.8271	0.8222	0.8175
0.1367	0.8439	0.8390	0.8348	0.8300	0.8254
0.1464	0.8477	0.8431	0.8388	0.8341	0.8295
0.1713	0.8576	0.8534	0.8489	0.8442	0.8400

TABLE II  
Parameters of Eq. (2) expressing the temperature dependence of density (in g/cm<sup>3</sup>) of a methanol-urea system of a given composition (w)

w	$a_1$	$-b_1 \cdot 10^4$	r
0.0502	1.08861	9.40	0.99963
0.0709	1.09171	9.26	0.99957
0.0854	1.10067	9.34	0.99931
0.1050	1.11396	9.50	0.99986
0.1199	1.11656	9.40	0.99946
0.1367	1.11812	9.20	0.99979
0.1464	1.11844	9.08	0.99991
0.1713	1.12246	8.88	0.99982

TABLE III

Parameters of Eq. (3) expressing the dependences of density (in g/cm<sup>3</sup>) on composition for methanol-urea systems at a constant temperature (K)

<i>T</i> , K	<i>a</i> <sub>2</sub>	<i>b</i> <sub>2</sub>	<i>r</i>
298·15	0·78617	0·4196	0·99984
303·15	0·78112	0·4225	0·99981
308·15	0·77690	0·4217	0·99989
313·15	0·77200	0·4227	0·99988
318·15	0·76647	0·4294	0·99993

TABLE IV

Dependence of heat capacities (in J/kg) of the methanol-urea system on temperature and composition

<i>T</i> , K	<i>w</i>				
	0·0502	0·1067	0·1410	0·1730	0·1811
298·15	2·39	2·26	2·35	2·54	2·57
303·15	2·42	2·30	2·38	2·57	2·60
308·15	2·46	2·33	2·42	2·61	2·64
313·15	2·50	2·36	2·45	2·65	2·68
318·15	2·53	2·40	2·48	2·69	2·71
323·15	2·57	2·44	2·52	2·73	2·75
328·15	2·61	2·48	2·56	2·77	2·79

TABLE V

Parameters of Eq. (4) expressing the temperature dependence of heat capacity of solutions of the methanol-urea systems at a constant composition

<i>w</i>	<i>a</i> <sub>3</sub>	<i>b</i> <sub>3</sub> · 10 <sup>3</sup>	<i>r</i>
0·0502	0·193	7·357	0·99929
0·1067	0·108	7·214	0·99848
0·1410	0·282	6·929	0·99878
0·1730	0·213	7·786	0·99936
0·1811	0·373	7·357	0·99929

and the dependences of the properties on composition usually have a sigmoid shape. A decrease followed by a growth of heat capacities in dependence on composition, as found for the methanol-urea system, has also been observed for the water-urea system. The increase in  $C_p^I$  with increasing temperature is similar for the two systems as well.

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