PHYSICO-CHEMICAL PROPERTIES OF THE TERNARY SYSTEM UREA–AMMONIUM NITRATE–WATER. DENSITY

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Density of the ternary system urea–ammonium nitrate–water was measured in the range of overall concentrations 0–75 mass % at temperatures of 0, 20, 30 and 40°C. The experimental data are compared with the values calculated from the relation obtained by combining the temperature dependences of densities of the binary systems urea–water and ammonium nitrate–water.

An extensive literature investigation showed that there exist nearly no data on physico-chemical properties of the ternary system urea–ammonium nitrate–water (hereinafter U–A–H_2O) though this system is interesting both from the point of view of industrial utilization and from the theoretical wiewpoint with regard to different nature of both components of the solution. Therefore we have measured some physico-chemical properties of this system. As the first of them, the density which is needed for the determination of further properties of the ternary system considered is presented.

EXPERIMENTAL

Chemicals used. Urea and ammonium nitrate, both of A.R. purity, Lachema, Brno and distilled water were used.

Measuring method. The Reichschauer pycnometers of volume 10 cm^3 were used for measuring the density. The solutions were prepared by weighing from chemicals dried over calcium chloride. The temperature in thermostat was maintained with an accuracy of $\pm 0{\cdot}03$°C. The mean error of experimental determination was $2 \cdot 10^{-4}$ g/cm^3.

By using this method, the density of both binary systems, *viz.* urea–water (hereinafter U–H_2O) and ammonium nitrate–water (hereinafter A–H_2O) and the density of the ternary system U–A–H_2O were measured as a function of concentration at temperatures of 0, 20, 30 and 40°C.

RESULTS

A number of data on the densities of the binary systems U–H_2O and A–H_2O in dependence on concentration and temperature were found in the literature[1–57]. It was

found out by a detailed critical analysis[58] that those data are of different quality. Since the aim of this work is the determination of physico-chemical properties of ternary or, if need be, multicomponent systems, if it is possible from the values of these properties for binary systems or, at least, the comparison of in such a way calculated values with experimental ones, also the values of densities of the binary systems were measured once again by the same method and at the same conditions as the densities of the ternary system. Our experimental values for temperatures of 0, 20, 30 and 40°C were treated along with the critically selected literature data for the temperature range of 0–100°C. The data for the U–H_2O binary system can be expressed by the quadratic equation

$$\varrho_U = \varrho_0 + a_U w_U + b_U w_U^2 , \qquad (1)$$

while for the representation of the data for the A–H_2O binary system, it is necessary to use the cubic equation

$$\varrho_A = \varrho_0 + a_A w_A + b_A w_A^2 + c_A w_A^3 . \qquad (2)$$

In these relations, ϱ_U, ϱ_A denote the density of the binary system U–H_2O and A–H_2O, respectively, ϱ_0 denotes the density of pure water at the temperature considered. The coefficients a, b, c which have dimension of density, are the following cubic functions of temperature

$$a_U = 2{\cdot}98212 \,.\, 10^{-3} - 1{\cdot}38830 \,.\, 10^{-5} t + 8{\cdot}26905 \,.\, 10^{-8} t^2 + 1{\cdot}13311 \,.\, 10^{-9} t^3 , \qquad (3)$$

$$b_U = 1{\cdot}09075 \,.\, 10^{-6} + 9{\cdot}87766 \,.\, 10^{-8} t + 1{\cdot}91592 \,.\, 10^{-11} t^2 - 1{\cdot}10193 \,.\, 10^{-11} t^3 , \qquad (4)$$

$$a_A = 4{\cdot}46026 \,.\, 10^{-3} - 2{\cdot}66502 \,.\, 10^{-5} t + 3{\cdot}68577 \,.\, 10^{-7} t^2 - 1{\cdot}91054 \,.\, 10^{-9} t^3 , \qquad (5)$$

$$b_A = 1{\cdot}60935 \,.\, 10^{-6} + 4{\cdot}00452 \,.\, 10^{-7} t - 7{\cdot}72281 \,.\, 10^{-9} t^2 + 4{\cdot}92713 \,.\, 10^{-11} t^3 , \qquad (6)$$

$$c_A = 8{\cdot}24773 \,.\, 10^{-8} - 1{\cdot}97529 \,.\, 10^{-9} t + 4{\cdot}47778 \,.\, 10^{-11} t^2 - 3{\cdot}12392 \,.\, 10^{-13} t^3 . \qquad (7)$$

Mean deviation of our experimental density data for the binary system U–H_2O from the data calculated from Eq. (*1*) with the coefficients in terms of Eqs (*3*) and (*4*) amounts to 0·019%. Mean deviation of experimental values for the binary system A–H_2O from the values calculated from Eqs (*2*) and (*5*)–(*7*) amounts to 0·027%.

The values of densities measured for the ternary system U–A–H_2O at temperatures of 0, 20, 30 and 40°C are given in Table I.

Attempting to calculate density of the ternary system from the data for binary

TABLE I

Density of the urea–ammonium nitrate–water ternary system

w_U, %	w_A, %	ϱ_{exp} g/cm^3	ϱ_{calc} g/cm^3	Δ, %	ϱ'_{calc} g/cm^3	Δ, %
			Temperature 0°C			
7·5043	2·5013	1·0333	1·0335	−0·02	1·0333	0·00
15·0120	5·0039	1·0671	1·0674	−0·03	1·0671	0·00
26·1248	8·7084	1·1181	1·1181	0·00	1·1181	0·00
37·4715	12·4905	1·1716	1·1705	0·09	1·1715	0·01
5·0061	5·0064	1·0373	1·0372	0·01	1·0371	0·02
9·9778	9·9777	1·0743	1·0747	−0·04	1·0744	−0·01
17·5303	17·5303	1·1327	1·1324	0·03	1·1322	0·04
25·0214	25·0214	1·1927	1·1907	0·17	1·1928	−0·08
30·5495	30·5497	1·2388	1·2346	0·34	1·2369	0·15
33·4953	33·4955	1·2648	1·2582	0·52	1·2617	0·24
2·5221	7·5676	1·0414	1·0413	0·01	1·0413	0·01
5·0005	15·0015	1·0822	1·0825	−0·03	1·0822	0·00
7·5276	22·5830	1·1247	1·1253	−0·03	1·1251	−0·04
8·7416	26·2249	1·1467	1·1462	0·04	1·1461	0·05
12·4960	37·4878	1·2147	1·2123	0·20	1·1234	0·11
13·7058	41·1180	1·2373	1·2343	0·24	1·2359	0·12
15·1361	45·4077	1·2656	1·2606	0·39	1·2630	0·20
16·7432	50·2283	1·2976	1·2909	0·52	1·2944	0·24
			Temperature 20°C			
3·3313	1·6657	1·0141	1·0141	0·00	1·0141	0·00
10 0045	4·9891	1·0462	1·0466	−0·04	1·0463	−0·01
18·5438	9·4325	1·0898	1·0902	0·04	1·0899	−0·01
20·0065	9·9772	1·0964	1·0968	−0·04	1·0966	−0·02
26·6031	13·3961	1·1313	1·1316	−0·03	1·1318	−0·04
33·4240	16·7278	1·1675	1·1675	0·00	1·1686	−0·09
39·9314	19·9660	1·2038	1·2030	0·07	1·2051	−0·17
46·5815	23·2908	1·2421	1·2401	0·16	1·2438	−0·14
2·5154	2·5155	1·0152	1·0154	−0·02	1·0154	−0·02
5·4968	5·4955	1·0359	1·0360	−0·01	1·0358	0·01
9·5177	9·5177	1·0640	1·0645	0·05	1·0641	−0·01
11·1268	11·1647	1·0757	1·0762	0·05	1·0759	−0·02
20·0178	19·9845	1·1414	1·1418	0·03	1·1420	−0·05
24·9635	24·8789	1·1803	1·1797	0·05	1·1807	−0·03
29·9910	29·9907	1·2218	1·2201	0·14	1·2223	−0·04
34·9408	34·9411	1·2643	1·2607	0·29	1·2644	−0·01

TABLE I
(*Continued*)

w_U, %	w_A, %	ϱ_{exp} g/cm^3	ϱ_{calc} g/cm^3	Δ, %	ϱ'_{calc} g/cm^3	Δ, %
1·6718	3·3436	1·0163	1·0165	−0·02	1·0165	−0·02
5·0007	9·9994	1·0532	1·0537	−0·05	1·0534	−0·02
10·0011	19·9984	1·1114	1·1119	−0·04	1·1117	−0·03
14·2689	28·5443	1·1641	1·1642	−0·01	1·1646	−0·04
16·6685	33·3254	1·1953	1·1945	0·07	1·1955	−0·02
19·9801	39·9583	1·2399	1·2379	0·16	1·2401	−0·02
23·3013	46·6029	1·2871	1·2831	0·31	1·2870	0·01
			Temperature 30°C			
7·5043	2·5013	1·0254	1·0255	−0·01	1·0253	0·01
15·0120	5·0039	1·0560	1·0563	−0·03	1·0560	0·00
22·6168	7·5391	1·0904	1·0885	0·17	1·0883	0·19
26·1248	8·7084	1·1036	1·1037	−0·01	1·1037	−0·01
29·9484	9·9826	1·1167	1·1205	−0·34	1·1207	−0·36
37·4715	12·4905	1·1540	1·1542	−0·02	1·1552	−0·10
46·5864	15·5287	1·1973	1·1964	0·08	1·1989	−0·13
50·1802	16·7267	1·2141	1·2134	0·06	1·2166	−0·20
56·2935	18·7645	1·2471	1·2429	0·34	1·2475	−0·03
5·0061	5·0064	1·0290	1·0290	0·00	1·0288	0·02
9·9778	9·9777	1·0634	1·0633	0·01	1·0629	0·05
15·0136	15·0142	1·0991	1·0992	−0·01	1·0990	0·01
17·5303	17·5303	1·1177	1·1177	0·00	1·1177	0·00
20·0203	20·0206	1·1360	1·1362	−0·02	1·1365	−0·04
25·0214	25·0214	1·1751	1·1745	0·05	1·1756	−0·04
30·5495	30·5497	1·2205	1·2184	0·17	1·2207	−0·02
33·4953	33·4955	1·2450	1·2425	0·20	1·2457	−0·06
37·4035	37·4028	1·2792	1·2752	0·31	1·2798	−0·03
37·4367	37·4370	1·2794	1·2755	0·31	1·2801	−0·05
2·5221	7·5676	1·0326	1·0328	−0·02	1·0326	0·00
5·0005	15·0015	1·0704	1·0707	−0·03	1·0704	0·00
7·5276	22·5830	1·1115	1·1110	0·05	1·1108	0·06
8·7416	26·2249	1·1314	1·1311	0·03	1·1310	0·04
9·9970	29·9900	1·1527	1·1522	0·04	1·1525	0·02
12·4960	37·4878	1·1967	1·1958	0·08	1·1968	−0·01
13·7058	41·1180	1·2189	1·2176	0·11	1·2192	−0·02
15·1361	45·4077	1·2461	1·2441	0·16	1·2464	−0·02
16·7432	50·2283	1·2777	1·2747	0·24	1·2780	−0·02
18·7346	56·2037	1·3188	1·3139	0·37	1·3187	0·01
18·7437	56·2310	1·3188	1·3141	0·36	1·3189	−0·01

TABLE I
(*Continued*)

w_U, %	w_A, %	ϱ_{exp} g/cm^3	ϱ_{calc} g/cm^3	Δ, %	ϱ'_{calc} g/cm^3	Δ, %
			Temperature 40°C			
7·5043	2·5013	1·0211	1·0212	−0·01	1·0211	0·00
15·0120	5·0039	1·0511	1·0513	−0·02	1·0509	0·02
26·1248	8·7084	1·0974	1·0976	−0·02	1·0976	−0·02
37·4715	12·4905	1·1479	1·1472	0·06	1·1482	−0·03
50·1802	16·7267	1·2072	1·2055	0·14	1·2086	−0·11
5·0061	5·0064	1·0247	1·0247	0·00	1·0246	0 01
9·9778	9·9777	1·0582	1·0582	0·00	1·0579	0·03
17·5303	17·5303	1·1117	1·1115	0·02	1·1115	0·02
25·0214	25·0214	1·1689	1·1674	0·13	1·1684	0·04
30·5495	30·5497	1·2147	1·2106	0·34	1·2129	0·15
33·4953	33·4955	1·2383	1·2344	0·32	1·2376	0·06
37·4367	37·4370	1·2726	1·2669	0·45	1·2716	0·08
2·5221	7·5676	1·0282	1·0285	−0·03	1·0284	−0·02
7·5276	22·5830	1·1058	1·1056	0·02	1·1054	0·04
8·7416	26·2249	1·1256	1·1254	0·02	1·1253	0·03
12·4960	37·4878	1·1905	1·1894	0·09	1·1905	0·00
13·7058	41·1180	1·2127	1·2112	0·12	1·2127	0·00
15·1361	45·4077	1·2395	1·2375	0·16	1·2398	−0·02
16·7432	50·2283	1·2709	1·2679	0·24	1·2712	−0·02
18·7346	56·2037	1·3118	1·3070	0·37	1·3118	0·00

systems only, several methods were tested. The empirical equation

$$\varrho_{calc} = \varrho_0 + a_A w_A + a_U w_U + (b_A^{1/2} w_A + b_U^{1/2} w_U)^2 + c_A w_A^3 \qquad (8)$$

was found to suit best. The coefficients a_A, a_U, b_A, b_U and c_A are given by Eqs (3)–(7). The symbols w_A, w_U denote mass per cent of ammonium nitrate (A) and urea (U) in the ternary solution (the same meaning have these symbols in Table I, too). Thus, Eq. (8) in combination with Eqs (3)–(7) allows to calculate density of the U–A–H_2O ternary system at any temperature within the range of 0–100°C and overall concentration of salts within 0–75 mass %. The values of density ϱ_{calc} calculated from the data for binary systems only in terms of Eq. (8) are given in the fourth column of Table I. In the fifth column there is the calculated value of per cent deviation of experimental data from the data calculated by means of Eq. (8), $\Delta = 100(\varrho_{exp} -$

$-\varrho_{calc})/\varrho_{calc}$. By analyzing the errors, it was found that the value of deviation is quadratic function of overall salt concentration in the system, $w = w_A + w_U$, and that the experimental data can be expressed by the relation

$$\varrho'_{calc} = \varrho_{calc}(1{\cdot}000237_3 - 5{\cdot}389 \,.\, 10^{-5}w + 1{\cdot}333 \,.\, 10^{-6}w^2)\,, \qquad (9)$$

where ϱ_{calc} is the density value calculated for the given ternary system in terms of Eq. (8). The values of ϱ'_{calc} calculated from Eq. (9), which was evaluated on the basis of experimental data for the U–A–H_2O ternary system given in Table I, are in the sixth column of this table. The seventh column gives the deviations of the measured data from those calculated in terms of Eq. (9).

From the comparison of the measured density values of the urea–ammonium nitrate–water ternary system (the mutual ratio of mass concentrations of dissolved components, w_U/w_A from 3 : 1 to 1 : 3) with the values calculated from empirical equations (8) and (9) follows: It is possible to calculate the density of the U–A–H_2O ternary system in terms of Eq. (8) on the basis of the knowledge of the concentration and temperature dependence of density for the binary systems U–H_2O and A–H_2O only. It is evident from the values of per cent deviations that the accuracy in the concentration range 0–50 mass % is very good (absolute value of mean deviation is 0·04%). Within the concentration range 50–75 mass %, the absolute value of mean deviation is 0·25%. This higher value is apparently due to the fact that, for both binary systems, this concentration region is already a region of supersaturated solutions, and the concentration and temperature dependences of densities of both binary systems are already extrapolated here.

Eq. (9), evaluated on the basis of experimental data for ternary system, yields the density values which differ from the experimental values in the region of concentrations of 0–50 mass % on the average by 0·03%, and, in the region of concentrations of 50–75 mass %, by 0·07%.

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