SATURATED VAPOUR PRESSURES OF THE TERNARY SYSTEM UREA–AMMONIUM NITRATE–WATER

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Saturated vapour pressures of the ternary liquid solutions of urea and ammonium nitrate in water were investigated by the isopiestic method at 15, 25 and 35°C. The measurements were carried out within the concentrations that are measurable by means of the NaCl standard solutions (i.e. up to the NaCl molality 6 mol/kg). The experimental data are correlated in terms of isotonic solutions of the urea–water and ammonium nitrate–water binary systems.

No data were found in the literature on the saturated vapour pressures of the liquid phase containing the components of the above-mentioned ternary system. With regard to the nature of components, it is always a case of the vapour pressure of water in the equilibrium vapour phase at usual conditions in this system even though recently some authors[1,2] have called attention to the possibility of urea occurrence in the vapour phase, and dealt quantitatively with the problem of its distribution factors. We took the results of their study as a basis to check the possible error which could arise from calculating the saturated vapour pressures over urea solutions in water considering only water in the vapour phase. We carried out checking calculations for the experimental values of saturated vapour pressures over the binary solutions of urea, given in the literature, e.g.[3-5]. These calculations proved that in the temperature range coming into consideration for our measurements $(0-35°C)$, the corrections for the urea transfer into the vapour phase are quite negligible, are deep below the limit of differences between the values of saturated vapour pressures given by different authors, and therefore they were not considered at all in our experiments.

From the methods which could be considered at the given temperatures, the isopiestic method (e.g.[6]) was chosen for the experimental determination of saturated vapour pressures of water in the system studied. It is relatively very accurate and more rapid than direct methods[6], moreover being less demanding on apparatus. However, the obtained results are not absolute; the saturated vapour pressures of solutions are determined according to the values for standard, simultaneously measured solutions, and depend on the correctness of those data. The measured data are therefore presented in the original ascertained form, i.e. the values of compositions of isopiestic solutions at a certain temperature.

For a rational course when measuring the ternary system, we exploited the knowledge published in a summary form in several works by Lenzi and coworkers[7,8]. These authors used a method enabling to correlate data in ternary systems in terms of data of the binary systems component––water which are in isopiestic equilibrium with the ternary solution. The method stems in principle from a linear relation between molalities of most binary aqueous solutions with the same saturated water vapour pressure (Zhdanovskii rule derived originally for electrolytes) and from the Robinson–Bower relation for vapour pressure lowering in ternary aqueous solutions[9]. In ternary systems, which the simplest variant of the procedure[7] mentioned can be applied to, it is possible to calculate directly the composition of ternary system at a chosen saturated vapour pressure only on the basis of concentrations of corresponding binary solutions at the same saturated vapour pressure and temperature. With more complicated types of ternary systems, it is necessary to know for such a calculation besides the data on saturated vapour pressures for the binary systems still at least several values of saturated vapour pressures determined experimentally for the ternary system. By choosing suitably the concentration of these measured ternary solutions, it is, of course, possible to reduce substantially their number. This way of correlating or interpolating the data is very suitable for isopiestic measurements because the experimental simultaneously measured points correspond always to the condition of identical saturated vapour pressure. The choice of solutions measured by us was therefore conformed to the mentioned method of treatment.

EXPERIMENTAL

Chemicals

As in our foregoing paper[10], substances of A.R. purity, after drying and without further purification, were used for measurement. This procedure coresponded to the accuracy with which the concentration of substances was determined in experiments. The solutions for the measurements were directly weighed, redistilled water being used.

Apparatus

A classical desiccator, tempered and exhaustible desiccator apparatus[6] with 24 gilded silver crucibles was used. The common practice of isopiestic method is to measure at the temperature of 25°C. The measurements at temperatures differing already by 10°C bring about difficulties. If we measure at higher temperatures, the problem is especially the condensation of water vapour from the gas phase in the desiccator during the experiment on the places where the temperature boundary is formed between the surface of tempering bath and neighbouring environment and the condensation on cooling after finishing the experiment. When measuring at low temperatures, the time needed for thorough equilibrating increases disproportionately, and the condensation of water vapour on undesirable places at the beginning of temperation takes place as well. In both the cases, also waste of time increases somewhat due to the necessity to wait a longer time before weighing the crucibles to equalize their experimental and laboratory temperatures.

Therefore we performed the measurements in the ternary system only at temperatures differing at most by ten degrees from the usual ambient temperature of 25°C after a preceding check with binary systems that the used usual experimental technique with small modifications[11] yielded even under these conditions sufficiently accurate results.

Sodium chloride was used as a reference standard. The results presented are average values of mostly three simultaneous determinations (at least of two, at most of five).

RESULTS AND DISCUSSION

When correlating data by the method[7] chosen it is substantial to know the dependence of the water activity (or of saturated vapour pressure at the given temperature) over the urea–water and ammonium nitrate–water binary solutions with relatively most considerable accuracy. In the literature there exist a number of older and newer works in which are available either the data on direct determination of saturated vapour pressures of these solutions at some concentrations or indirect data, *i.e.* quantities from which the saturated vapour pressure over the solutions can be calculated. These data, which, however, are not always mutually consistent, were critically evaluated and processed[12] into the form of dependences of the saturated vapour pressures on molalities of solutions for different temperature levels. The equations obtained, though they render the behaviour of binary solutions in a wide range of variables relatively very well, fail in their mutual combination, which is necessary for calculating the ternary data, as an exact basis of calculation. For our purpose and temperature interval, only isopiestic data[13–17] proved to be sufficiently accurate from the literature values. These isopiestic data for binary solutions were determined experimentally only at 25°C except several data in the work[16] (values at 0°C).

Therefore both the binary systems were measured, too, at 15 and 35°C, simultaneously with a checking measurement at 25°C (ref.[12]) whose results were compared with the literature values. The resulting values of molalities of urea $(m_{0,U})$ and ammonium nitrate $(m_{0,A})$ in binary solutions at different temperatures and activities of water are given in Table I. They were found on the basis of smoothed experi-

TABLE I

Isopiestic molalities of urea $(m_{0,U})$ and ammonium nitrate $(m_{0,A})$ at activity of water a_w in the binary solutions at different temperatures — smoothed values

a_w	15°C		25°C		35°C	
	$m_{0,U}$	$m_{0,A}$	$m_{0,U}$	$m_{0,A}$	$m_{0,U}$	$m_{0,A}$
0·975	1·482	0·839	1·465	0·829	1·419	0·802
0·950	3·213	1·866	3·139	1·822	3·090	1·792
0·925	5·103	3·032	4·948	2·936	4·906	2·909
0·900	6·997	4·236	6·887	4.165	6·762	4·085
0·875	9·001	5·539	8·966	5·516	8·862	5·448
0·850	11·187	6·990	11·054	6·888	10·997	6·863
0·825	13·456	8·523	13·290	8·410	13·167	8·326
0·800	15·783	10·119	15·649	10·027	15·550	9·965
0·775	18·242	11·828	18·027	11·677	18·003	11·661

mental dependences of isopiestic molalities of solutions of both substances and sodium chloride as the standard. The activities of water corresponding to the solutions of the standard, and presented in Table II, were read for the temperature of 25°C by interpolation from the data of ref.[6]; the osmotic coefficients given in recent critically processed literature[18] were taken as the basis of their calculations for 15 and 35°C. These last data have naturally lower accuracy than the values for 25°C.

For further continuation according to the chosen method of correlation, it was necessary to find out what type of ternary system[7] the solutions of urea with ammonium nitrate correspond to. The basic type can be described in the simplest way as the case for which holds the equation

$$[a_w, t] \qquad m_1 = m_{0,1} - m_{0,1} m_2 / m_{0,2} , \qquad (1)$$

where subscripts 1 and 2 stand for dissolved substances, the molalities m_i refer to ternary system, the molalities $m_{0,i}$ to binary system, both for the same value of activity of water a_w and temperature t. To describe more complicated systems with more expressive interactions of components in solution, it is necessary to use more complex equations than Eq. (1) containing empirical constants which are functions of a_w and m_i.

To check whether our system satisfies the basic type, three sets of solutions with different ratio of components at three somewhat different activities of water at 25°C were measured. The results summarized in Table III show that Eq. (1) is fulfilled very well for the system studied under the conditions given.

TABLE II

Molalities of NaCl in the binary solutions for chosen activities of water (a_w) obtained from literature data by interpolation[6] (for 25°C) and by calculation from osmotic coefficients[18] (for 15 and 35°C)

a_w	15°C	25°C	35°C
0·975	0·760	0·752	0·731
0·950	1·51	1·485	1·46
0·925	2·23	2·175	2·16
0·900	2·86	2·831	2·79
0·875	3·47	3·460	3·43
0·850	4·07	4·035	4·02
0·825	4·64	4·600	4·57
0·800	5·18	5·150	5·13
0·775	5·71	5·665	5·66

TABLE III

Isopiestic molalities in the ternary solutions of different molalities of urea (m_U) and nitrate (m_A) at activity of water a_w — experimental data

$t = 25°C$		
a_w	m_U	m_A
0·854	0·000	6·739
	0·779	6·157
	1·042	6·022
	5·154	3·521
	9·698	0·687
	9·856	0·636
	10·810	0·000
0·851	0·000	6·827
	0·791	6·252
	1·051	6·091
	5·200	3·553
	9·852	0·700
	9·949	0·641
	10·944	0·000
0·847	0·000	6·998
	0·808	6·406
	1·079	6·249
	5·343	3·652
	10·066	0·714
	10·210	0·658
	11·199	0·000

$t = 15°C$		
a_w	m_U	m_A
0·852	0·000	6·914
	0·816	6·458
	1·087	6·295
	5·334	3·646
	9·994	0·710
	10·045	0·647
	10·986	0·000
0·851	0·000	6·834
	0·820	6·492
	1·091	6·313
	5·346	3·652
	10·020	0·711
	10·096	0·651
	10·953	0·000

For the possibility of general use of Eq. (I), we checked still thoroughly its validity by measuring a number of equimolal solutions of urea (molality m_U) with nitrate (m_A) approximately in the range of molalities $0.2 - 10$; provided some deviations from Eq. (I) occur, they should be rather substantial for mixtures with this ratio of components especially at higher concentrations. The results of measurement at all three temperatures are given in Table IV as pairs of molalities of isopiestic

TABLE IV

Isopiestic molalities of the standard solutions of NaCl (m_{NaCl}) and of the equimolal ternary solutions of urea and nitrate ($m_U = m_A$), experimental ($m_S = m_U = m_A$) and calculated from independent data for binary solutions ($m_\Sigma = m_U = m_A$); deviation $\Delta \% = 100(m_\Sigma - m_S)/m_S$

m_{NaCl}	m_S	m_Σ	$\Delta \%$
		$t = 15°C$	
0.154	0.101	0.100	−1.22
1.359	1.045	1.038	−0.67
1.746	1.406	1.402	−0.32
2.066	1.726	1.727	0.03
2.246	1.927	1.919	−0.39
2.320	2.002	2.001	−0.06
2.420	2.093	2.113	0.93
3.271	3.131	3.159	0.90
3.313	3.149	3.215	2.10
		$t = 25°C$	
0.127	0.089	0.082	−8.07
0.165	0.110	0.107	−2.85
0.511	0.356	0.348	−2.25
1.405	1.073	1.080	0.62
1.441	1.094	1.112	1.62
1.502	1.135	1.168	2.95
2.300	1.930	1.978	2.48
2.350	1.989	2.034	2.26
3.169	3.026	3.025	−0.03
3.307	3.140	3.207	2.13
3.997	4.165	4.191	0.62
4.247	4.522	4.577	1.22
4.303	4.611	4.666	1.19
4.461	4.895	4.921	0.53
4.508	4.977	5.000	0.46

	m_{NaCl}	m_S	m_Σ	$\Delta \%$
			$t = 35°C$	
	0·156	0·102	0·101	−0·98
	0·517	0·353	0·352	−0·28
	0·545	0·369	0·373	1·08
	2·550	2·230	2·261	1·39
	3·075	2·960	2·903	−1·92
	3·275	3·075	3·164	2·89
	3·297	3·203	3·194	−0·28
	3·527	3·439	3·508	2·00
	3·614	3·505	3·630	3·57
	3·682	3·605	3·727	3·38
	3·743	3·681	3·815	3·64
	3·802	3·770	3·901	3·47
	3·832	3·811	3·941	3·41
	3·914	3·921	4·066	3·71
	3·945	3·981	4·113	3·30
	4·475	4·785	4·943	3·30
	4·660	5·080	5·251	3·37

solutions standard (m_{NaCl})–equimolal ternary mixtures $(m_S = m_U = m_A)$. The table gives also the values of molalities of equimolal ternary mixture (m_Σ) calculated from Eq. (1) for the given isopiestic molality of the standard and their percent deviations $\Delta (\%)$ from the experimental value $(\Delta = 100(m_\Sigma - m_S)/m_S)$. The values $m_{0,U}$ and $m_{0,A}$ needed for inserting into Eq. (1) when calculating m_Σ were read from the dependences $m_{0,U}$ and $m_{0,A}$ on the molality m_{NaCl} for the corresponding temperatures according to Tables I and II. Relatively very good agreement of the experimental values m_S with those calculated quite independently of the experimental data for the ternary mixtures proves the applicability of the described expression of the properties in ternary system on the basis of data for the binary subsystems in terms of Eq. (1) at all the temperatures observed and in the entire concentration range of solutions of the standard, i.e. practically up to saturated solutions of urea in water.

For a chosen saturated vapour pressure of water over the ternary solution falling into the interval for which binary data are known (Table I), it is then possible to determine in terms of Eq. (1) the concentrations of the ternary solution of urea and nitrate with arbitrary mutual ratio of both these components. The back procedure, i.e. the calculation of saturated vapour pressure over the ternary solutions of urea and

nitrate with a chosen mutual ratio and overall concentration is numerically more demanding because it in substance means to find, on the basis of values m_U and m_A, such a pair of values $m_{0,U}$ and $m_{0,A}$ that should satisfy Eq. (1) for the given temperature. This seeking must be carried out either numerically by successive approximations or by graphic interpolation in a prepared dense network of straight lines representing dependence (1). If it is not a question of a single calculation, it is therefore obviously more advantageous to use the first procedure, $i.e.$ to calculate the concentra-

TABLE V

Isopiestic molalities of the standard solutions of NaCl (m_{NaCl}), binary solutions of urea ($m_{0,U}$) and nitrate ($m_{0,A}$), equimolal ternary solutions of urea and nitrate ($m_U = m_A$), experimental ($m_S = m_U = m_A$) and calculated from experimental values $m_{0,U}$ and $m_{0,A}$ ($m'_S = m_U = m_A$); deviation $\Delta\% = 100(m'_S - m_S)/m_S$

m_{NaCl}	$m_{0,U}$	$m_{0,A}$	m_S	$m_{S'}$	Δ, %
		$t = 15°C$			
0·187	0·346	0·195	0·124	0·125	0·57
1·000	2·030	1·165	0·741	0·740	−0·10
1·511	3·216	1·880	1·184	1·186	0·20
1·844	4·072	2·392	1·505	1·507	0·13
2·286	5·292	3·141	1·962	1·971	0·46
3·198	8·148	4·995	3·092	3·097	0·15
		$t = 25°C$			
0·120	0·222	0·124	0·084	0·080	−5·28
0·137	0·253	0·144	0·094	0·092	−2·37
0·149	0·277	0·159	0·101	0·101	0·01
0·498	0·973	0·544	0·350	0·349	−0·31
4·016	10·991	6·795	4·191	4·199	0·19
		$t = 35°C$			
0·176	0·320	0·178	0·111	0·114	2·70
0·467	0·909	0·512	0·330	0·327	−0·75
0·812	1·594	0·845	0·557	0·552	−0·90
3·385	8·645	5·185	3·290	3·241	−1·48
3·574	9·240	5·545	3·458	3·465	0·21
3·652	9·513	5·715	3·548	3·570	0·62
3·775	9·953	5·999	3·721	3·743	0·59
3·868	10·289	6·230	3·873	3·880	0·19
4·009	10·800	6·554	4·047	4·079	0·78

tions m_U and m_A in solution for the chosen saturated vapour pressures and the chosen ratio of urea to nitrate, and, if need be, to interpolate between these values.

As it was mentioned above, the accuracy of calculated concentrations for ternary system depends substantially on the accuracy of values of molalities of binary solutions which are in isopiestic equilibrium with the ternary system. Therefore, the sets of ternary solutions were still measured at all the temperatures simultaneously with both the binary systems at the same value of molality of the standard. In this way

TABLE VI

Saturated vapour pressures of water p_w over the ternary equimolal solutions of urea and nitrate (m_S) from Table V; the values of saturated vapour pressures of pure water p_w^0 from ref.[20]

m_S	a_w	p_w, Pa
$t = 15°C\,(p_w^0 = 1\,704·93\,Pa)$		
0·124	0·9938	1 694·7
0·741	0·9672	1 649·0
1·184	0·9500	1 619·7
1·505	0·9397	1 602·1
1·962	0·9227	1 573·1
3·092	0·8861	1 510·7
$t = 25°C\,(p_w^0 = 3\,167·21\,Pa)$		
0·084	0·9960	3 154·5
0·094	0·9952	3 152·0
0·101	0·9947	3 150·4
0·350	0·9832	3 114·0
4·191	0·8507	2 694·3
$t = 35°C\,(p_w^0 = 5\,622·87\,Pa)$		
0·111	0·9937	5 587·4
0·330	0·9837	5 531·2
0·557	0·9720	5 465·4
3·290	0·8767	4 929·6
3·458	0·8685	4 883·5
3·548	0·8652	4 864·9
3·721	0·8600	4 835·7
3·873	0·8561	4 813·7
4·047	0·8502	4 780·6

a test was carried out whether it is possible to attain still better agreement of experimental values of molalities of equimolal ternary mixtures (m_S) with the theoretical values (m'_s) calculated in terms of Eq. (1), this time on the basis of $m_{0,U}$ and $m_{0,A}$ determined simultaneously experimentally. The results of these experiments and calculations are given in Table V along with the deviations calculated similarly as in Table IV. It is evident from the comparison of these deviations with those in Table IV that their values reduced as expected. This is in harmony with the fact that the experimental values $m_{0,i}$ used here are subjected to a smaller error than those used in Table IV which were obtained by extrapolating the quite independent data from Tables I and II.

In the last Table VI, the concrete values of saturated vapour pressures for equimolal ternary solutions from Table V are given for completeness as they were calculated on the basis of simultaneously measured molalities of the standard. The dependence of activity of water (a_w) on molality of NaCl corresponds to the data from Table II. Saturated vapour pressures p_w over the solution were calculated on the basis of saturated vapour pressures of pure water p_w^0 at the same temperature, from the relation $p_w = a_w p_w^0$ without corrections for nonideality[19] in both phases. These corrections are negligible under the given conditions, as we found out by a checking calculation. The values of p_w^0 were taken from standard literature[20] after converting to Pa.

CONCLUSION

On the basis of a number of measured equimolal mixtures at three temperature levels it was proved experimentally that the ternary system urea–ammonium nitrate–water pertains, in the range of water activities of $1{\cdot}0$ to $0{\cdot}85$, to the type of systems in which it is possible to calculate in terms of Eq. (1) its isopiestic molalities on the basis of those in binary systems (here urea–water and ammonium nitrate–water). When knowing the values of saturated vapour pressures of water for those binary systems, one knows as well the saturated vapour pressures over the ternary system. In view of the simple dependences of the experimental data on concentration and temperature, it is possible to take into account that the conclusions given here hold reliably even for mildly extrapolated values of variables.

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