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Solubility and Thermodynamics of Solvation of Krypton in Aqueous-Methanol Solutions of Urea at 101325 Pa and 278–318 K

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Abstract—The solubility of krypton in the liquid system $H_2O–CH_3OH–CO(NH_2)_2$ was measured at 101325 Pa and 278.15–318.15 K (10 K step) in the whole range of compositions of the mixed aqueous-methanol solvent at the urea content of up to 1.5 solvomolality units (mole fraction 0.0263). The temperature dependence of the Sechenov parameter of the solubility of the noble gas exhibits an inversion in the region of equimolar composition of the water–methanol mixture. A considerable decrease in the salting-out of the gas with urea in this concentration region is due to loosening of the solvation shell of urea.

Studying thermodynamic properties of solutions of biomolecules in water and mixed aqueous-organic systems furnishes important information on the role of these compounds in physiological processes, and the results of such studies are used in pharmaceutical industry [1].

Urea $CO(NH_2)_2$ is a biologically important and active substance, being one of the major participants and products of the activity of a human body [2]. This is one of the reasons why studies of urea in the pure (crystalline) form and in solutions are urgent and numerous. Studying the effect of temperature and various additives on the structural and thermodynamic characteristics of urea solutions in liquid systems with hydrogen bonding furnishes information necessary not only for understanding the structure of these solutions, but also for elucidating the nature of hydrophilic interactions in peptides and proteins [3].

In this connection, it is interesting to study aqueous-methanol solutions of urea, in view of two facts. First, planar $CO(NH_2)_2$ molecules can form with an aqueous environment (at $T > 308$ K) structures "topologically complementary" to the solvent in the bulk [2]. Second, urea exhibits "negative partial expansibility" in methanol [4]. The nature of these effects is directly associated with the character of intermolecular interactions, depending in the nonadditive manner on the composition of the water–methanol mixture [5]. The structure-oriented interpretation of such dependences on the supramolecular level requires experimental approaches that furnish sufficient information but, at the same time, do not exert strong perturbing effects on the system.

One of the best approaches is studying the solubility of a noble gas, which does not react chemically with the solution components, in a one- or multicomponent system [6, 7]. The noble gas atoms have sperical shape and relatively low polarizability, which is favorable for using them as probes, from the viewpoint of the solution structure and solvation of the noble gas [6, 8]. The low solubility of the gas in polar liquids allows partial leveling of structural macroeffects induced by changes in the interparticle interactions in the system under the influence of the dissolved probe.

In this study, we measured the solubility and calculated the standard thermodynamic functions of solvation (solution) of Kr (hereinafter, A1) in solutions of urea $CO(NH_2)_2$ (hereinafter, A2) in methanol CH_3OH (hereinafter, L2) and its mixtures with water H_2O (hereinafter, L1) of the compositions $[(1 - X_{L2}) + X_{L2}]$ (hereinafter, solvents L), where X_{L2} is the mole fraction of methanol. The measurements were made at 278.15, 288.15, 298.15, 308.15, and 318.15 K in the range of A2 concentrations of 0–1.5 solvomolality units $c_{sm,A}$.[1] The choice of the solvomolal concentration scale for describing the solubility was repeatedly substantiated previously [8–10]. The solubility data are listed in Table 1.

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[1] The solvomolality $c_{sm,A}$ is a dimensionless parameter of the solution composition, expressing the concentration of component A: $c_{sm,A} = (n_A/n_L) \times 55.50843$, where n_A and n_L are the amounts (moles) of the solute and solvent. The normalizing factor 55.50843 is numerically equal to the amount of H_2O (moles) in 1000 g of water.

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Table 1. Solubility of Kr ($c_{sm,A1} \times 10^3$) at 101 325 Pa and 278.15–318.15 K in aqueous-methanol solutions of urea[a]

$c_{sm,A2}$	T, K	Composition of water–methanol mixture, X_{L2}					
		0	0.06	0.1	0.3	0.6	1.0
0	278.15	4.183	4.844	4.940	7.000	20.27	61.44
	288.15	3.158	3.780	4.026	6.457	19.58	57.84
	288.15	2.500	3.095	3.435	6.085	18.99	54.57
	308.15	2.063	2.639	3.044	5.853	18.51	51.65
	318.15	1.769	2.336	2.787	5.716	18.10	49.06
0.1	278.15	4.138	4.796	4.901	6.978	20.22	61.24
	288.15	3.127	3.747	3.997	6.439	19.52	57.62
	298.15	2.478	3.071	3.413	6.069	18.93	54.33
	308.15	2.047	2.621	3.026	5.839	18.45	51.40
	318.15	1.757	2.322	2.772	5.703	18.04	48.80
0.2	278.15	4.094	4.750	4.865	6.958	20.17	61.05
	288.15	3.097	3.716	3.970	6.422	19.47	57.41
	298.15	2.457	3.049	3.393	6.055	18.88	54.11
	308.15	2.031	2.605	3.010	5.827	18.39	51.16
	318.15	1.745	2.309	2.759	5.692	17.98	48.54
0.5	278.15	3.976	4.623	4.767	6.906	20.04	60.52
	288.15	3.017	3.630	3.900	6.380	19.34	56.83
	298.15	2.401	2.988	3.341	6.019	18.74	53.47
	308.15	1.990	2.561	2.969	5.797	18.24	50.47
	318.15	1.714	2.276	2.725	5.665	17.83	47.82
1.0	278.15	3.818	4.446	4.644	6.851	19.90	59.79
	288.15	2.911	3.513	3.815	6.339	19.19	56.00
	298.15	2.328	2.908	3.281	5.988	18.57	52.56
	308.15	1.939	2.505	2.925	5.771	18.06	49.48
	318.15	1.678	2.237	2.691	5.644	17.64	46.76
1.5	278.15	3.702	4.312	4.568	6.835	19.85	59.25
	288.15	2.837	3.428	3.770	6.334	19.12	55.35
	298.15	2.280	2.853	3.253	5.988	18.49	51.81
	308.15	1.908	2.471	2.910	5.777	17.96	48.65
	318.15	1.659	2.217	2.684	5.655	17.52	45.87

[a] $X_{A1} = c_{sm,A1}/(55.50843 + c_{sm,A1})$.

To calculate the thermodynamic functions of solvatin of A1, we used a procedure [11] based on a physically substantiated mathematical model adequately fitting the temperature dependence of the solubility of a gaseous substance that does not chemically react with the solvent:

$$R\ln c_{sm,A1} = a_0 + a_1 u_1 + a_2 u_2. \quad (1)$$

Here $u_1 = (T - \theta)/T$, $u_2 = \theta/T + \ln(T/\theta) - 1$, where θ is a temperature arbitrarily chosen within the measurement range. The coefficients a_i are independent of each other and correspond in the physical sense to the standard molar thermodynamic functions of solvation (solution) of a gas at a temperature θ: $-\Delta_{solv}G^0_{A1}(\theta) = a_0\theta$, $\Delta_{solv}H^{\infty}_{A1}(\theta) = a_1\theta$, $\Delta_{solv}S^0_{A1}(\theta) = a_0 + a_1$, and $\Delta_{solv}C_{p,A1}(\theta) = a_2$. The quantities $\Delta_{solv}Y^{\infty}_{A1}$ (where Y is H or C_p) refer to infinite dilution, according to the standardization conditions. The standard thermodynamic functions of solvation of Kr in solvents L of variable composition and in solutions L + A2 at $c_{sm,A2}$ 1.5, calculated by Eq. (1), are listed in Table 2.

As seen from the $c_{sm,A1}$ data in Table 1, the solubility of Kr decreases with an increase in the A2 concentration and in temperature. Actually, in the entire range of compositions of L, urea acts as a salting-out agent relative to Kr. With an increase in X_{L2}, $c_{sm,A1}$ sharply increases. Additions of A2 weaken the influence of both alcohol content and temperature on the solubility of A1.

Table 2 shows that $\Delta_{solv}G^0_{A1}$ is positive in the

Table 2. Thermodynamic characteristics of the solvation of Kr in water–methanol–urea mixtures at $c_{sm,A2}$ 0 and 1.5[a]

X_{L2}	$c_{sm,A2}$	T, K	$\Delta_{solv}G^0_{A1}$, kJ mol^{-1}	$\Delta_{solv}H^{\infty}_{A1}$, kJ mol^{-1}	$-T\Delta_{solv}S^0_{A1}$, kJ mol^{-1}	$\Delta_{solv}C^{\infty}_{p,A1}$, J mol^{-1} K^{-1}	X_{L2}	$c_{sm,A2}$	T, K	$\Delta_{solv}G^0_{A1}$, kJ mol^{-1}	$\Delta_{solv}H^{\infty}_{A1}$, kJ mol^{-1}	$-T\Delta_{solv}S^0_{A1}$, kJ mol^{-1}	$\Delta_{solv}C^{\infty}_{p,A1}$, J mol^{-1} K^{-1}
0	0	278.15	12.65	19.79 ± 0.14	32.45 ± 0.14		0.3	0	278.15	11.47	5.95 ± 0.07	17.43 ± 0.07	
		288.15	13.79	17.74 ± 0.08	31.53 ± 0.08				288.15	12.08	4.79 ± 0.04	16.86 ± 0.04	
		298.15	14.85	15.69 ± 0.04	30.54 ± 0.04	205 ± 7			298.15	12.64	3.62 ± 0.02	16.26 ± 0.02	117 ± 4
		308.15	15.84	13.64 ± 0.09	29.48 ± 0.09				308.15	13.17	2.45 ± 0.04	15.62 ± 0.04	
		318.15	16.77	11.59 ± 0.15	28.35 ± 0.15				318.15	13.66	1.28 ± 0.08	14.94 ± 0.08	
	1.5	278.15	12.95	18.77 ± 0.07	31.72 ± 0.07			1.5	278.15	11.53	5.65 ± 0.09	17.18 ± 0.09	
		288.15	14.05	16.68 ± 0.04	30.73 ± 0.04				288.15	12.13	4.52 ± 0.05	16.64 ± 0.05	
		298.15	15.08	14.58 ± 0.02	29.66 ± 0.02	209 ± 3			298.15	12.69	3.38 ± 0.03	16.07 ± 0.03	113 ± 4
		308.15	16.04	12.49 ± 0.04	28.53 ± 0.04				308.15	13.21	2.25 ± 0.06	15.45 ± 0.06	
		318.15	16.93	10.39 ± 0.07	27.33 ± 0.07				318.15	13.69	1.11 ± 0.10	14.80 ± 0.10	
0.06	0	278.15	12.32	17.59 ± 0.06	29.91 ± 0.06		0.6	0	278.15	9.01	2.42 ± 0.04	11.43 ± 0.04	
		288.15	13.36	15.40 ± 0.03	28.76 ± 0.03				288.15	9.42	2.24 ± 0.02	11.66 ± 0.02	
		298.15	14.32	13.22 ± 0.02	27.54 ± 0.02	219 ± 3			298.15	9.82	2.06 ± 0.01	11.88 ± 0.01	18 ± 2
		308.15	15.21	11.03 ± 0.04	26.24 ± 0.04				308.15	10.22	1.87 ± 0.03	12.09 ± 0.03	
		318.15	16.02	8.84 ± 0.06	24.87 ± 0.06				318.15	10.61	1.69 ± 0.04	12.30 ± 0.04	
	1.5	278.15	12.60	16.34 ± 0.02	28.93 ± 0.02			1.5	278.15	9.06	2.60 ± 0.05	11.67 ± 0.05	
		288.15	13.60	14.19 ± 0.01	27.79 ± 0.01				288.15	9.48	2.45 ± 0.03	11.93 ± 0.03	16 ± 2
		298.15	14.53	12.04 ± 0.01	26.57 ± 0.01	215 ± 1			298.15	9.89	2.29 ± 0.01	12.18 ± 0.01	
		308.15	15.38	9.90 ± 0.01	25.28 ± 0.01				308.15	10.30	2.13 ± 0.03	12.43 ± 0.03	
		318.15	16.17	7.75 ± 0.02	23.91 ± 0.02				318.15	10.70	1.97 ± 0.05	12.67 ± 0.05	
0.1	0	278.15	12.28	14.61 ± 0.14	26.89 ± 0.14		1.0	0	278.15	6.45	4.03 ± 0.07	10.48 ± 0.07	
		288.15	13.21	12.47 ± 0.08	25.68 ± 0.08				288.15	6.83	4.09 ± 0.04	10.91 ± 0.04	
		298.15	14.07	10.33 ± 0.04	24.39 ± 0.04	214 ± 7			298.15	7.21	4.15 ± 0.02	11.35 ± 0.02	–6 ± 4
		308.15	14.85	8.18 ± 0.09	23.03 ± 0.09				308.15	7.59	4.21 ± 0.05	11.80 ± 0.05	
		318.15	15.56	6.04 ± 0.16	21.60 ± 0.16				318.15	7.97	4.27 ± 0.08	12.24 ± 0.08	
	1.5	278.15	12.46	13.72 ± 0.016	26.18 ± 0.16			1.5	278.15	6.53	4.54 ± 0.09	11.08 ± 0.09	
		288.15	13.37	11.65 ± 0.09	25.02 ± 0.09				288.15	6.93	4.64 ± 0.05	11.57 ± 0.05	
		298.15	14.20	9.58 ± 0.05	23.78 ± 0.05	207 ± 8			298.15	7.34	4.73 ± 0.03	12.06 ± 0.03	–9 ± 5
		308.15	14.96	7.51 ± 0.10	22.47 ± 0.10				308.15	7.74	4.82 ± 0.06	12.56 ± 0.06	
		318.15	15.66	5.44 ± 0.18	21.10 ± 0.18				318.15	8.15	4.91 ± 0.10	13.06 ± 0.10	

[a] The error of calculating $\Delta_{solv}G^0_{A1}$ does not exceed ±5 J mol^{-1}.

entire range of temperatures and compositions and regularly increases with an increase in the content of A_2 and in temperature; the influence of $c_{sm,A2}$ is weak. Additions of alcohol cause a monotonic decrease in $\Delta_{solv}G^0_{A1}$. The enthalpy ($\Delta_{solv}H^{\infty}_{A1}$) and entropy ($T\Delta_{solv}S^0_{A1}$) constituents of $\Delta_{solv}G^0_{A1}$ are negative. The first term appreciably decreases in the absolute value with increasing temperature in the water-rich range and slightly increases at X_{L2} ~1.0 (Table 2). The second term varies only slightly. It is important that the term $|T\Delta_{solv}S^0_{A1}|$ appreciably exceeds (especially at high T) the term $|\Delta_{solv}H^{\infty}_{A1}|$ and, in contrast to the latter term, at X_{L2} ~0.6 increases with temperature, i.e., the dissolution of Kr in the systems under consideration is entropy-controlled.

It is also interesting that the plot of $\Delta_{solv}H^{\infty}_{A1}$ vs. X_{L2} at 278 K has a flat maximum in the concentration region close to equimolar composition of L; with increasing temperature, this maximum shifts toward water-rich compositions. Additions of A2 do not noticeably affect the positions of these maxima. Significant differences between $\Delta_{\mathrm{solv}}H^{\infty}_{\mathrm{A1}}$ ($c_{\mathrm{sm,A2}}$ 0) and $\Delta_{\mathrm{solv}}H^{\infty}_{\mathrm{A1}}$($c_{\mathrm{sm,A2}}$ 1.5) are observed only in the range of X_{L2} from 0 to ~0.15 (at 318 K) or to 0.3 (at 278 K).

In this connection, it is appropriate to analyze the entropy characteristics of solvation of A1 in the mixtures under consideration on the basis of a model [12] developed in [10], according to which $\Delta_{\mathrm{solv}}G^{0}_{\mathrm{A1}}$ can be considered as a sum of three terms:

$$\Delta_{\mathrm{solv}}S^{0}_{\mathrm{A1}} = \Delta S^{0}_{\mathrm{I,A1}} + \Delta S^{0}_{\mathrm{IIa}} + \Delta S^{0}_{\mathrm{IIb}}$$

The first term (negative) corresponds to the entropy of transfer of 1 mol of a gas from the ideal gas phase to solution, determined by restriction of the translation motion in a dense solvent medium (in our case, L + A2). The second and third terms correspond, respectively, to the change in the solvent entropy due to its structural rearrangement under the influence of dissolved gas species and to the total change in the entropy of the gas and solvent due to interaction of their molecules.

As shown in [10], the contribution $\Delta S^{0}_{\mathrm{I,A1}}$ is virtually independent of the solvent and temperature and amounts to ~50 J mol^{-1} K^{-1}. The dependence of $\Delta S^{0}_{\mathrm{II}} = \Delta S^{0}_{\mathrm{IIa}} + \Delta S^{0}_{\mathrm{IIb}}$ on the solvent composition at 278.15 and 318.15 K is illustrated by Fig. 1. It is seen that the strongest influence on $\Delta S^{0}_{\mathrm{II}}$ is exerted by the alcohol concentration. At $X_{\mathrm{L2}} > 0.45$ (T 278.15 K) and $X_{\mathrm{L2}} > 0.22$ (T 318.15 K), $\Delta S^{0}_{\mathrm{II}}$ is positive. The temperature effect is clearly manifested up to X_{L2} ~0.6. Additions of urea appreciably affect $\Delta S^{0}_{\mathrm{II}}$ only in the ranges $0 \le X_{\mathrm{L2}} \le 0.3$ and $0.6 \le X_{\mathrm{L2}} \le 1.0$. In the first range, $\Delta S^{0}_{\mathrm{II}}$ grows (becomes more positive) in the presence of A2, and in the second range it decreases. At X_{L2} ~0.45 (T 278.15 K) or ~0.22 (T 318.15 K), $\Delta S^{0}_{\mathrm{II}}$($c_{\mathrm{sm,A2}}$ 0) ≈ $\Delta S^{0}_{\mathrm{II}}$($c_{\mathrm{sm,A2}}$ 1.5).

Following Krestov's views [12], we can assume that, in the composition range $0 \le X_{\mathrm{L2}} < 0.3$ (water-rich region), Kr dissolves by the intercalation mechanism, with the prevalence of the effects from stabilization of the structure of the mixed solvent, whereas at $X_{\mathrm{L2}} > 0.6$ (alcohol-rich region) Kr dissolves by the solvation mechanism, but the effects from structure break ($\Delta S^{0}_{\mathrm{II}} > 0$) prevail over the effects from the solvation interaction. In the intermediate composition range ($0.3 < X_{\mathrm{L2}} < 0.6$), these mechanisms compete, and $\Delta S^{0}_{\mathrm{II}}$ in the middle of this range is close to zero.

Unfortunately, it is impossible now to estimate quantitatively the contributions $\Delta S^{0}_{\mathrm{IIa}}$ and $\Delta S^{0}_{\mathrm{IIb}}$. However, the dependence of $\Delta S^{0}_{\mathrm{II}}$ on X_{L2} in the water-rich composition range of L suggests the prevailing role of structural transformations of the solvent in the course of solvation of A1, as influenced by temperature and organic additives.

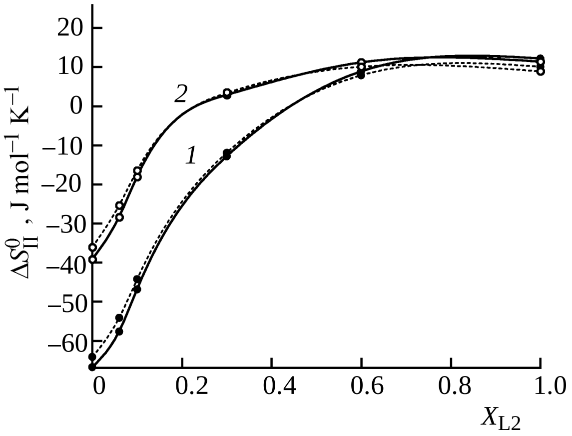

Fig. 1. "Structural" contribution to the entropy constituent of the standard Gibbs energy of solvation of Kr in the liquid system water–methanol–urea as a function of the alcohol concentration at $c_{\mathrm{sm,A2}}$ (solid line) 0 and (dotted line) 1.5. (*1*) 278.15 K and (*2*) 318.15 K.

To analyze the effect of additions of A2 on the solubility of A1 and obtain additional information on the interparticle interactions in the forming multicomponent system, we calculated the standard Sechenov solubility parameters K^{0}_{S} characterizing the influence exerted on the solubility of a component by another component. The procedure for determining K^{0}_{S} was described in detail elsewhere [13]. Here we give only the main thermodynamic relationships.

The transfer of 1 mol of A1 from a standard solution in solvent L of a composition [(1 – X_{L2}) + X_{L2}] into a standard (with respect to A1) solution of the composition [(1 – X_{L2}) + X_{L2} + $c_{\mathrm{sm,A2}}$] can be expressed by

$$K^{0}_{S} = \lim_{(c_{\mathrm{A1}} \to c_{\mathrm{A1}} = 1,\ \mathrm{hyp.})} \left(\frac{\partial \ln c_{\mathrm{sm,A1}}}{\partial c_{\mathrm{sm,A2}}} \right)_{\mu^{0}_{\mathrm{A1}}}$$

The values of K^{0}_{S} are given in Table 3.

The quantity K^{0}_{S} is related to the standard Gibbs energy of transfer of 1 mol of A1 from a standard (ideal infinitely dilute) solution in L to a standard solution in (L + A2) (with the total amounts of components L remaining unchanged) by Eq. (2) [14, 15]:

$$\Delta_{\mathrm{tr}}G^{0}(\mathrm{A1,L} \to \mathrm{L} + \mathrm{A2}) = -RTK^{0}_{S}c_{\mathrm{sm,A2}}. \qquad (2)$$

According to the McMillan–Mayer theory, for the standard state holds

Table 3. Standard Sechenov parameters ($-K_S^0 \times 10^3$) of the solubility of Kr in water–methanol–urea mixtures

T, K	Composition of water–methanol mixture, X_{L2}					
	0	0.06	0.1	0.3	0.6	1.0
278.15	111.3 ± 0.7	101.6 ± 0.8	80.8 ± 0.5	32.6 ± 0.3	27.1 ± 0.9	33.2 ± 0.2
288.15	101.3 ± 0.3	89.1 ± 0.6	73.8 ± 0.5	29.6 ± 0.3	29.1 ± 1.2	38.3 ± 0.3
298.15	90.7 ± 0.5	78.4 ± 0.5	65.1 ± 0.4	27.1 ± 0.5	31.2 ± 0.8	43.7 ± 0.6
308.15	81.9 ± 0.8	68.4 ± 0.8	59.8 ± 0.6	24.7 ± 0.5	33.9 ± 0.5	49.2 ± 0.4
318.15	72.9 ± 1.3	60.6 ± 1.0	54.9 ± 0.5	23.5 ± 0.4	34.5 ± 0.7	54.4 ± 0.3

$$\Delta_{tr}G^0_{A1} = 2c_{sm,A2}g_{A1A2}. \quad (3)$$

In Eq. (3), g_{A1A2} is the parameter (of the Gibbs energy) of the pair interaction between solvated particles A1 and A2.

From Eqs. (2) and (3) follows

$$g_{A1A2} = -RTK_S^0/2.$$

The dependence of g_{A1A2} on T and composition of L is shown in Fig. 2.

By approximating the temperature dependence of g_{A1A2} by an empirical equation given below, we calculated, using the known thermodynamic relationships, the enthalpy (h_{A1A2}) and entropy [s_{A1A2}, (Ts_{A1A2})] coefficients of pair interaction at 298.15 K (Table 4).

$$g_{A1A2} = \sum_{i=0}^{2} a_i(T - 298.15)^i.$$

As follows from Table 3 and Fig. 2, the quantities K_S^0 and g_{A1A2} depend in a complex manner on the composition of the water–methanol mixture and on temperature, passing through a minimum in the region of the equimolar ratio of L1 and L2. In the same region, the temperature gradient of g_{A1A2} and the interaction parameters h_{A1A2} and s_{A1A2} change sign.

The positive values of g_{A1A2} (Table 4) indicate that the transfer of 1 mol of Kr from a water–methanol mixture of a given composition to the mixture of the same composition but also containing urea is thermodynamically hindered owing to the mutual repulsion of the solvated A1 atoms and A2 molecules. With an increase in temperature, g_{A1A2} decreases in the water-rich region and increases in the alcohol-rich region of compositions.

Figure 3 shows a 3*D* diagram of the dependences of the volume coefficients of pair interaction of solvated A2 molecules in water–methanol mixtures on

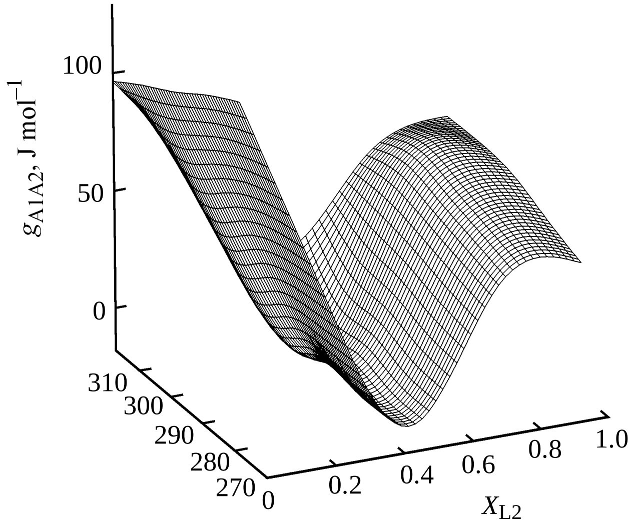

Fig. 2. Parameter of the Gibbs energy of the pair interaction krypton–urea, g_{A1A2}, in the water–methanol mixture as a function of the solvent composition and temperature.

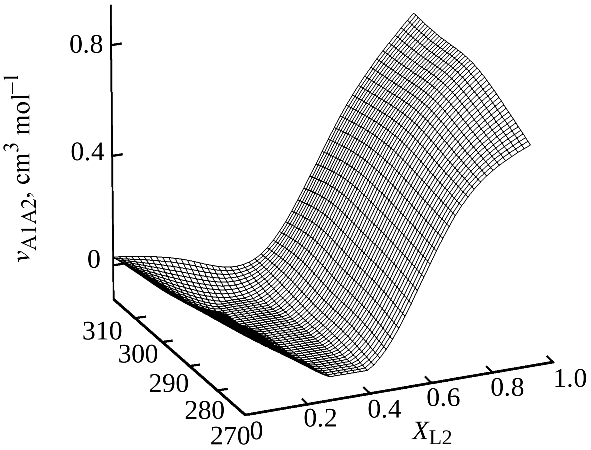

Fig. 3. Volume virial coefficient of the pair interaction urea–urea, v_{A1A2}, in the water–methanol mixture as a function of the solvent composition and temperature.

the composition and temperature. The diagram was plotted on the basis of data from [5]. It was concluded in [5] that, on the whole, the structure of the solvation shell of urea (without taking into account its composition in detail) in a water–methanol mixture att X_{L2} ~0.5 is looser than the structure of the solvent in the bulk. An apparent analogy between the 3D diagrams shown in Figs. 2 and 3 indicates that the features of intermolecular interactions A1–A2 in water–methanol mixtures, revealed in this study, are largely determined by the solvent packing in the urea solvation shell.

Unfortunately, our data do not allow us to judge what is the composition of local environments (solvation aggregates) of solutes A1 and A2 in mixed solvent L and how their composition varies with X_{L2}. However, presumably, a significant decrease in the salting-out effect of urea at X_{L2} ~0.5 is associated with the “looser” structure of its solvation shell at these compositions with the strongly fluctuating structure (according to [16]). This fact makes the urea molecules more accessible to interaction with Kr atoms, which is well consistent with the above conclusion that the constituents of ΔS^0_{II} in the range $0.3 < X_{L2} < 0.6$ compensate each other.

Thus, we have convincingly showed that urea is complementarily incorporated in the structure of not only water but also water–methanol mixtures, at least up to methanol mole fraction of ~0.3–0.5.

EXPERIMENTAL

Krypton was of ultrapure grade (main substance content ≥99.9978%). Water of natural isotope composition was deionized and double-distilled in a Pyrex apparatus, with addition of $KMnO_4$ in the first distillation. The specific electrical conductivity of water was ~1.3 μS cm^{-1}. Methanol of chemically pure grade was purified by refluxing with magnesium methylate, followed by distillation; the mole fraction of the main substance in the purified product was 0.99982, as determined by Fischer titration and densimetry. Urea of ultrapure grade was used without additional purification; it was dried for 48 h in a vacuum at 335 K and stored in a vacuum desiccator over a P_2O_5 bed. All manipulations with the alcohol were performed in a dry box. Urea solutions were prepared gravimetrically from degassed components in special evacuated mixers, accurate to within $\sim 1.0 \times 10^{-4}$ $c_{\text{sm,A2}}$ unit. The degassing procedure is described in detail elsewhere [17].

The solubility was measured at a Kr partial pressure of 101 325 Pa by the saturation method on a precision microgasometric unit [17] equipped with a ~10 cm^3 absorption vessel. The measurement procedure is discussed in detail elsewhere [17].

Table 4. Thermodynamic parameters of the pair interaction A1–A2 at 298 K[a]

X_{L2}	g_{A1A2}, J mol^{-1}	s_{A1A2}, J mol^{-1} K^{-1}	Ts_{A1A2}, J mol^{-1}	h_{A1A2}, J mol^{-1}
0	113(0.2)	0.81(0.02)	242	355(5)
0.06	97(0.2)	0.94(0.01)	279	376(3)
0.1	81(0.2)	0.54(0.03)	160	241(9)
0.3	33(0.2)	0.17(0.01)	51	84(5)
0.6	39(0.3)	–0.36(0.03)	–108	–69(8)
1.0	54(0.2)	–0.84(0.01)	–251	–197(2)

[a] In parentheses are the standard deviations.

The gas solubility was expressed in the form of equilibrium (corrected for the nonideality) Bunsen absorption coefficients β of gas A1 in solvent L, in accordance with Eq. (4) [17]:

$$\beta_{A1} = v_{A1}(T, p) \times 273.15 z_{A1}(\text{n.c.})/[v_L(T, p) T z_{A1}(T, p)], \quad (4)$$

where $v_{A1}(T, p)$ is the volume of the pure gas absorbed at the experimental temperature T and pressure p (equal to the partial pressure p_{A1} 101 325 Pa); $v_L(T, p)$, volume of the degassed solvent (or solution); and $z_{A1}(T, p)$ and $z_{A1}(\text{n.c.})$ (n.c. denotes normal conditions), compressibility coefficients of Kr in the gas phase, calculated by the Lee–Kessler method [18]. Solvent L is either pure water (L1) or methanol (L2), or mixtures of the composition $[(1 - X_{L2}) + X_{L2} + c_{\text{sm,A2}}]$.

The accuracy of β_{A1} was evaluated by comparing our data on the solubility of oxygen (recommended gasometric reference [19]) in water with the most reliable published data [20]. To make the results more reliable, we made repeated measurements of the solubility of A1 in L1; the β_{A1} values were reproducible within ±0.2%, with no noticeable fixed errors. The choice of β_{A1} as the initial parameter for expressing the solubility in other units and for calculating the thermodynamic characteristics of solvation is governed by the experimental conditions (the partial pressure of the gas, p_{A1}, was not measured) and by the fact that the Bunsen coefficient by definition [21] is independent of p_{A1} and always refers to p_{A1} 101 325 Pa.

The data given in Table 1 for the solubility of Kr in solutions of urea in water–methanol mixtures are expressed in the form of the solvomolality coefficients $c_{\text{sm,A1}}$, which were calculated as follows:

$$c_{\mathrm{sm,A1}} = [\beta_{\mathrm{A1}}(55.50843\bar{M}_{\mathrm{L}} + c_{\mathrm{sm,A2}}M_{\mathrm{A2}})/(V^*_{\mathrm{A1}}\rho_{\mathrm{L}}),$$

where $\bar{M}_{\mathrm{L}} = [M_{\mathrm{L1}}(1 - X_{\mathrm{L2}}) + M_{\mathrm{L2}}X_{\mathrm{L2}}]$ is the mean molar weight of the solvent of the composition $[(1 - X_{\mathrm{L2}}) + X_{\mathrm{L2}}]$; M_{L1}, M_{L2}, and M_{A2} are, respectively, the molar weights of water, methanol, and urea; V^*_{A1} 22 388 $\mathrm{cm}^3\ \mathrm{mol}^{-1}$ [21] is the real molar volume of Kr under normal conditions; and ρ_{L} is the solvent density. The densities of the solutions under consideration were reported previously [5].

All the molar quantities were calculated using the IUPAC Table [22] of relative atomic weights [A_r(H) 1.00794, A_r(O) 15.9994, A_r(N) 14.00674, A_r(C) 12.01110].

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