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Thermodynamics of H/D Isotope Effects in Urea Hydration and Structural Features of Urea Aqueous Solutions at Various Temperatures: III.[1] Solubility of Argon and Krypton at 101 325 Pa in the Systems $H_2O–CO(NH_2)_2$ and $D_2O–CO(ND_2)_2$

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Abstract—The thermodynamic characteristics of hydration of Ar and Kr were calculated from experimental data on the solubility of Ar and Kr in solutions of urea in H_2O and of deuterourea in D_2O at 101 325 Pa and 278.15–318.15 K. Solutions of Ar and Kr significantly differ in the value of thermodynamic effects accompanying dissolution.

Our previous studies [1, 2] of the influence of temperature and isotope composition of the solvent on the volume properties of solutions of urea in H_2O and deuterourea in D_2O convincingly demonstrate that the method of H/D isotope substitution furnishes rich information on hydration and interparticle interactions in a solvent–solute system. At the same time, as shown in [3–5], still more information can be derived by using isotope substitution in combination with measuring the solubility of noble gases in the solutions under consideration.

A saturated solution of a noble gas is a sort of “indicator system” for revealing and quantitatively evaluating the thermodynamic effects related to the influence of the molecular composition, temperature, and pressure on the macroscopic state of an aqueous medium. This is due to specific features of hydrophobic hydration of gas molecules and to their relatively low concentration in saturated aqueous solution. The latter fact allows us to exclude from consideration, when analyzing the thermodynamic functions of solution of the indicator component, the contributions related to changes in interparticle interactions in the system under the influence of the added indicator.

In this work we determined the solubilities and thermodynamic functions of solution of Ar and Kr (hereinafter, A1) in solutions of $CO(NH_2)_2$ (hereinafter, $A2_H$) in water with natural isotopic abundance (L_H) and of $CO(ND_2)_2$ ($A2_D$) in D_2O (L_D). Measurements were performed at 278.15, 283.15, 288.15, 298.15, 308.15, and 318.15 K in the A2 ($A2_H$ or $A2_D$) concentration range c_{sm} 0–1.5 (solvomolality units). By definition [3], solvomolality is a rational dimensionless parameter of the solution composition given by the formula

$$c_{sm,\mathrm{A}} = 55.50843(n_\mathrm{A}/n_\mathrm{L}), \qquad (1)$$

where n_A and n_L are amounts of the solute A and solvent L (moles). The term 55.50843 [numerically equal to the amount of H_2O (moles) in 1000 g of water] was introduced as normalizing parameter for conveniency sake, because in this case for protic aqueous solutions the solvomolality $c_{sm,\mathrm{A}}$ becomes numerically equal to the molality $c_{m,\mathrm{A}}$. The molality scale is widely used in solution thermodynamics. At the same time, the use of the solvomolality scale is of principal importance for adequate interpretation of the thermodynamic functions of transfer, because, when these parameters are reduced to the solvomolality scale, in going from one solvent to another the ratio of the numbers of particles of solution components remains constant, and the so-called cratic factor is zero. If necessary, the concentrations on the solvomolality scale can be readily converted to mole fractions:

$$x_\mathrm{A} = c_{sm,\mathrm{A}}/(c_{sm,\mathrm{A}} + 55.50843). \qquad (2)$$

The data on solubilities of noble gases A1 in the systems $[L_H + A2_H]$ and $[L_D + A2_D]$ are listed in Table 1. For a more convenient comparison of the

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[1] For communication II, see [1].

Table 1. Parameters of Eqs. (3) and (4) for fitting the data on solubility of Ar and Kr (in the forms of $c_{sm,\mathrm{A1}}$ and x_{A1}) in the systems (S) H_2O–$CO(NH_2)_2$ (**I**) and D_2O–$CO(ND_2)_2$ (**II**)[a]

Gas (A1)	S	T, K	$c^*_{sm,\mathrm{A1}} \times 10^3$	$-a_1 \times 10^5$	$a_2 \times 10^5$	$x^*_{\mathrm{A}_1} \times 10^5$	$-b_1 \times 10^5$	$b_2 \times 10^4$
Ar	**I**	283.22	1.870	50.6 (0.5)	16.8 (0.4)	3.369	51.3 (0.4)	95.7 (1.8)
		288.17	1.681	39.2 (0.6)	12.9 (0.4)	3.028	39.6 (0.5)	73.2 (2.1)
		298.15	1.397	22.4 (0.3)	7.2 (0.2)	2.517	22.7 (0.3)	40.8 (1.2)
		308.25	1.206	10.5 (0.2)	3.0 (0.2)	2.173	10.7 (0.2)	17.1 (1.0)
		318.17	1.083	2.7 (0.2)	0.2 (0.2)	1.951	2.7 (0.2)	0.8 (1.1)
	II	283.22	2.087	58.3 (0.6)	16.9 (0.4)	3.760	58.9 (0.5)	94.8 (2.1)
		288.17	1.845	45.1 (0.6)	13.0 (0.4)	3.324	45.6 (0.5)	73.3 (2.0)
		298.15	1.498	25.8 (0.2)	7.2 (0.2)	2.699	26.1 (0.2)	40.8 (0.9)
		308.25	1.272	13.2 (0.2)	3.5 (0.1)	2.291	13.2 (0.2)	18.9 (0.8)
		318.17	1.129	4.7 (0.3)	0.8 (0.2)	2.034	4.8 (0.2)	3.9 (1.0)
Kr	**I**	278.15	4.183	43.9 (0.2)	8.2 (0.2)	7.535	44.1 (0.3)	44.4 (1.3)
		288.15	3.158	30.0 (0.2)	6.0 (0.1)	5.689	30.2 (0.2)	32.7 (0.8)
		298.15	2.500	21.1 (0.2)	4.5 (0.2)	4.504	21.4 (0.2)	25.0 (1.0)
		308.15	2.063	16.3 (0.2)	4.1 (0.2)	3.716	16.3 (0.2)	22.5 (0.7)
		318.15	1.769	12.1 (0.1)	3.3 (0.1)	3.187	12.2 (0.1)	18.6 (0.5)
	II	278.15	4.602	50.7 (0.2)	7.8 (0.2)	8.290	51.0 (0.3)	41.6 (1.3)
		288.15	3.438	34.7 (0.1)	5.7 (0.1)	6.193	34.9 (0.1)	30.4 (0.3)
		298.15	2.705	24.4 (0.2)	4.2 (0.1)	4.873	24.6 (0.2)	22.9 (0.9)
		308.15	2.218	18.0 (0.2)	3.4 (0.1)	3.996	18.2 (0.1)	18.3 (0.5)
		318.15	1.902	13.8 (0.1)	2.9 (0.1)	3.426	13.8 (0.2)	15.6 (0.6)

[a] The standard deviations are given in parentheses.

dependences of $c_{sm,\mathrm{A1}}$ and x_{A1} on the concentration of $\mathrm{A2}_{\mathrm{H(D)}}$ in the ranges $0 < c_{sm,\mathrm{A2}} < 1.5$ and $0 < x_{\mathrm{A2}} < 0.263$, the solubility data for A1 were approximated by the following equations:

$$\Delta c_{sm,\mathrm{A1}} = c_{sm,\mathrm{A1}} - c^*_{sm,\mathrm{A1}} = \sum_{i=1}^{n} a_i (c_{sm,\mathrm{A2}})^i, \qquad (3)$$

$$\Delta x_{\mathrm{A1}} = x_{\mathrm{A1}} - x^*_{\mathrm{A1}} = \sum_{i=1}^{n} b_i (x_{\mathrm{A2}})^i. \qquad (4)$$

Here, the parameters $c^*_{sm,\mathrm{A1}}$ (x^*_{A1}) refer to water isotopomers.

The error in $c_{sm,\mathrm{A1}}$ (x_{A1}) values calculated by Eqs. (3) and (4) does not exceed the error of our experimental data on the gas solubility (≤0.3%).

The quantity $c_{sm,\mathrm{A1}}$ was calculated as follows:

$$c_{sm,\mathrm{A1}} = [\beta_{\mathrm{A1}}(55.50843 M_{\mathrm{L}} + c_{sm,\mathrm{A2}} \mathrm{M}_{\mathrm{A2}})]/(V^*_{\mathrm{A1}} \rho_{\mathrm{A2,L}}), \qquad (5)$$

where β_{A1} is the Bunsen absorption coefficient of gas A1 in the solvent L(+A2), M_{L} and M_{A2} are the molar weights of the solvent and solute, V^*_{A1} is the true molar volume of the gas under normal conditions, and $\rho_{\mathrm{A2,L}}$ is the density of the solution [L + A2]. The density data were reported elsewhere [2]. The procedure for determining the Bunsen absorption coefficients is briefly given in the Experimental.

It should be noted that the choice of β_{A1} as the initial parameter for expressing the solubility (in the form of $c_{sm,\mathrm{A1}}$ or x_{A1}) and thermodynamic characteristics of solvation of A1 is not occasional. By definition [6, 7], the Bunsen absorption coefficient is a dimensionless quantity independent of the gas partial pressure over the solution. Therefore, with the choice of β_{A1}, there is no need in determining the equilibrium composition of the vapor–gas mixture over the solution, which considerably simplifies the experiment. This is a major advantage of expressing the solubility in such a form.

The choice of a mathematical model adequately reproducing the temperature dependence of the solubility of a gas A1 that does not react chemically with the solvent is very important. This problem is usually solved by known methods of linear regression analysis [8, 9], including least-squares smoothing regularization [10]. However, full consistency of the model with the experiment is not attained.

As concluded in [11], one of the main conditions for efficient calculation of thermodynamic characteristics of gas solution is construction of a mathematical model whose parameters would be mutually independent and would have a certain physical sense. The simplest and most adaptable solution is provided by expansion of the quantities $\Delta_{\mathrm{solv}}H^{\infty}_{\mathrm{A1}}(T)$ and $\Delta_{\mathrm{solv}}C^{\infty}_{\mathrm{p\ A1}}(T)$ in a Taylor series in a certain arbitrarily chosen reference temperature Θ. The thermodynamic essence of the model is given by the equation

$$R\ln c_{sm,\mathrm{A1}} = e_0 + e_1[(T - \Theta)/T] + e_2[\Theta/T + \ln(T/\Theta) - 1]. \qquad (6)$$

The coefficients e_i in Eq. (6) are mutually independent and correspond in their physical sense to the standard molar thermodynamic functions of gas solution at temperature Θ: $e_0 = -\Delta_{\mathrm{solv}}G^{0}_{\mathrm{A1}}(\Theta)/\Theta$, $e_1 = \Delta_{\mathrm{solv}}H^{\infty}_{\mathrm{A1}}(\Theta)/\Theta$, $e_0 + e_1 = \Delta_{\mathrm{solv}}S^{0}_{\mathrm{A1}}(\Theta)$, $e_2 = \Delta_{\mathrm{solv}}C^{\infty}_{p,\mathrm{A1}}$ [11] (the values of $\Delta_{\mathrm{solv}}H^{\infty}_{\mathrm{A1}}$ and $\Delta_{\mathrm{solv}}C^{\infty}_{p,\mathrm{A1}}$ refer to infinite dilution according to the standardization conditions). One of the most critical procedures for checking the reliability of the solubility data and adequacy of the chosen mathematical model is comparison of the values of $\Delta_{\mathrm{solv}}H^{\infty}_{\mathrm{A1}}$ calculated from the solubility data with those measured by a direct procedure (e.g., calorimetrically).

The molar thermodynamic parameters of solution of Ar and Kr in the systems $[\mathrm{L_H} + \mathrm{A2_H}]$ and $[\mathrm{L_D} + \mathrm{A2_D}]$ at various temperatures are listed in Table 2. Their comparison shows that the values of $\Delta_{\mathrm{solv}}H^{\infty}_{\mathrm{A1}}(c_{sm,\mathrm{A2}} = 0)$, calculated from our and published [5, 12, 13, 15, 19–21] solubility data and measured by precision calorimetry [14, 16–18], are mutually consistent. It is also important that the values of $\Delta_{\mathrm{solv}}C^{\infty}_{p,\mathrm{A1}}$, which are actually the second derivatives of $\Delta_{\mathrm{solv}}G^{0}_{\mathrm{A1}}$ with respect to temperature, are also fairly close. Our data on $\Delta_{\mathrm{solv}}G^{0}_{\mathrm{A1}}$ and $\Delta_{\mathrm{solv}}S^{0}_{\mathrm{A1}}$ cannot be compared with published data, because the numerical values of these functions depend on the way of expressing the concentration [3].

The isotope effects (functions of transfer) can be readily found as the differences between the corresponding thermodynamic functions of solution of A1 in solvents $\mathrm{L_H}(+\mathrm{A2_H})$ and $\mathrm{L_D}(+\mathrm{A2_D})$ by the formula

$$\Delta_{\mathrm{tr}}\Delta_{\mathrm{solv}}F_{\mathrm{A1,L_H}\to\mathrm{L_D}} = \Delta_{\mathrm{solv}}F_{\mathrm{A1,L_D}} - \Delta_{\mathrm{solv}}F_{\mathrm{A1,L_H}}, \qquad (7)$$

where F can stand for G, H, S, or C_p.

To calculate the isotope effects we used data from Tables 1 and 2. In [1, 2], we considered transfer of urea $[\mathrm{A2_{H(D)}}]$ from one solvent ($\mathrm{L_H}$) into another ($\mathrm{L_D}$). This transfer involved isotope substitution in both the solvent and solute molecules. In the case considered in this paper, noble gas atoms are transferred from the protium system $[\mathrm{L_H} + \mathrm{A2_H}]$ into the deuterium system $[\mathrm{L_D} + \mathrm{A2_D}]$, which simplifies interpretation of the isotope effects.

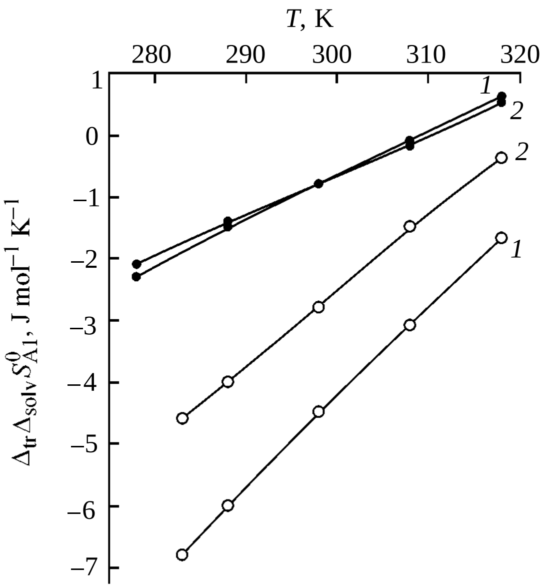

Fig. 1. Isotope effect in the entropy of solution of (light circles) Ar and (dark circles) Kr as a function of temperature T at $c_{sm,\mathrm{A2}}$ (*1*) 0 and (*2*) 1.5.

The isotope effects in the thermodynamic functions of solution (solvation) furnish valuable information on macroscopic changes produced by solute molecules in a solvent. In deriving such information, an important role is played by analysis of the quantities $\Delta_{\mathrm{tr}}\Delta_{\mathrm{solv}}S^{0}_{\mathrm{A1}}$, characterizing, on the whole, variation of the extent of structurization (ordering) of a liquid system under the influence of deuterium substitution.

Figure 1 shows the temperature dependences of the isotope effects in the entropy of solution of Ar and Kr. Figure 1 and Table 2 show that Ar, compared to Kr, is characterized by a several times greater isotope effect in the entropy of solution, although $|\Delta_{\mathrm{solv}}S^{0}_{\mathrm{Kr}}| > |\Delta_{\mathrm{solv}}S^{0}_{\mathrm{Ar}}|$. This fact shows that in hydration of Kr the structural differences between the solvent [L(+A2)] isotopomers are not manifested, and the structures formed around the Kr atom in the protium and deuterium systems are probably ordered to a similar extent. The same conclusion was made in [22] on the basis of data (obtained using Ben-Naim's approach [23]) on the variation of the average number of hydrogen bonds in aqueous solution at hydration of A1 gas molecules. The stronger binding of water molecules in the hydration shell of Kr is also indicated by the fact that, as the temperature is increased from 283 to 318 K, $\Delta_{\mathrm{solv}}S^{0}_{\mathrm{Kr}}$ changes by only ~2 J mol^{-1} K^{-1}, whereas $\Delta_{\mathrm{solv}}S^{0}_{\mathrm{Ar}}$ changes by 5 J mol^{-1} K^{-1} (Fig. 1).

Table 2. Standard molar thermodynamic characteristics of solution of Ar and Kr in H/D isotopomers of water and in aqueous solutions (S) of urea (**I**) and deuterourea (**II**) with $c_{sm,\mathrm{A2}}$ 1.5[a]

Gas (A1)	S	T, K	$c_{sm,\mathrm{A1}}$	$\Delta_{\mathrm{solv}}G^0_{\mathrm{A1}}$[b], kJ/mol	$-\Delta_{\mathrm{solv}}H^{\infty}_{\mathrm{A1}}$, kJ/mol	$-\Delta_{\mathrm{solv}}S^0_{\mathrm{A1}}$, kJ/mol	$\Delta_{\mathrm{solv}}C^{\infty}_{p,\mathrm{A1}}$[c], J mol^{-1} K^{-1}
Ar	**I**	283.15	0	14.784	15.32 ± 0.16, 14.95 [12]	106.3 ± 0.6	
			1.5	15.324	10.51 ± 0.08	91.3 ± 0.3	
		288.15	0	15.306	14.26 ± 0.12, 13.94 [13], 13.96 ± 0.09 [14]	102.6 ± 0.4	
			1.5	15.773	9.63 ± 0.06	88.2 ± 0.2	
		298.15	0	16.296	12.13 ± 0.05, 11.97 ± 0.18 [15], 12.27 ± 0.12 [12], 11.96 [13], 12.01 ± 0.08 [14], 11.94 ± 0.05 [16], 12.07 ± 0.16 [17], 12.0 ± 1.0 [18]	95.3 ± 0.2	213 ± 9, 200 ± 5 [14]
			1.5	16.624	7.86 ± 0.02	82.1 ± 0.1	177 ± 5
		308.15	0	17.213	9.99 ± 0.09, 10.14 [15], 10.10 [13], 9.97 ± 0.17 [14]	88.3 ± 0.3	
			1.5	17.416	6.09 ± 0.04	76.3 ± 0.1	
		318.15	0	18.062	7.86 ± 0.18	81.5 ± 0.6	
			1.5	18.150	4.31 ± 0.09	70.6 ± 0.3	
	II	283.15	0	14.526	17.49 ± 0.04	113.1 ± 0.2	
			1.5	15.169	11.99 ± 0.22	95.9 ± 0.8	
		288.15	0	15.080	16.21 ± 0.03, 16.81 [5], 15.95 [19]	108.6 ± 0.1	
			1.5	15.640	10.92 ± 0.16	92.2 ± 0.6	
		298.15	0	16.122	13.65 ± 0.01, 12.56 [5], 13.69 [13], 13.88 [20], 13.49 [21]	99.8 ± 0.1	256 ± 3
			1.5	16.525	8.78 ± 0.07	84.9 ± 0.2	214 ± 13
		308.15	0	17.078	11.08 ± 0.02, 11.17 [21]	91.4 ± 0.1	
			1.5	17.338	6.65 ± 0.12	77.8 ± 0.4	
		318.15	0	17.951	8.52 ± 0.05, 8.31 [5], 8.85 [21]	83.2 ± 0.2	
			1.5	18.082	4.50 ± 0.25	71.0 ± 0.8	
Kr	**I**	278.15	0	12.666	19.76 ± 0.05, 20.00 [15]	116.6 ± 0.2	
			1.5	12.948	18.77 ± 0.07	114.0 ± 0.2	
		288.15	0	13.795	17.71 ± 0.03, 17.52 ± 0.13 [14]	109.3 ± 0.1	
			1.5	14.051	16.68 ± 0.04	106.6 ± 0.1	
		298.15	0	14.853	15.65 ± 0.02, 15.61 ± 0.06 [15], 15.70 ± 0.13 [17], 15.28 ± 0.04 [16], 15.29 ± 0.06 [14]	102.3 ± 0.1	206 ± 3, 210 ± 3 [15], 220 ± 4 [14]
			1.5	15.082	14.58 ± 0.02	99.5 ± 0.1	210 ± 4
		308.15	0	15.842	13.60 ± 0.03, 13.12 ± 0.09 [14]	95.5 ± 0.1	
			1.5	16.042	12.49 ± 0.04	92.6 ± 0.1	
		318.15	0	16.764	11.54 ± 0.06	89.0 ± 0.2	
			1.5	16.934	10.39 ± 0.07	85.9 ± 0.2	
	II	278.15	0	12.445	20.56 ± 0.23	118.7 ± 0.8	
			1.5	12.759	19.60 ± 0.28	116.3 ± 1.0	
		288.15	0	13.591	18.31 ± 0.12, 17.22 [5], 18.40 [19], 19.44 [20]	110.7 ± 0.4	
			1.5	13.881	17.29 ± 0.15	108.1 ± 0.5	
		298.15	0	14.660	16.07 ± 0.07, 15.54 [5], 16.09 [19], 16.00 [20]	103.1 ± 0.2	225 ± 11
			1.5	14.924	14.98 ± 0.09	100.3 ± 0.3	231 ± 16
		308.15	0	15.653	13.82 ± 0.14, 13.85 [5], 13.78 [19]	95.7 ± 0.5	
			1.5	15.888	12.67 ± 0.18	92.7 ± 0.6	
		318.15	0	16.574	11.58 ± 0.25, 12.17 [5], 11.46 [19]	88.5 ± 0.8	
			1.5	16.778	10.35 ± 0.31	85.3 ± 1.0	

[a] All the values (except those given with a reference) were obtained in this work. [b] The confidence range (2σ) of the calculated values is within ±7 kJ/mol. [c] The values of $\Delta_{\mathrm{solv}}C^{\infty}_{p,\mathrm{A1}}$ are equal at all the temperatures, because the accuracy attained in the solubility measurements allows the use of only the three-parameter form of Eq. (6) [11].

Table 3. Standard values of the Sechenov parameters of the solubility of Ar and Kr in the systems (S) $H_2O–CO(NH_2)_2$ (**I**) and $D_2O–CO(ND_2)_2$, and the coefficients $\omega_1 = s_{A1A2}$ (J mol^{-1} K^{-1}) of Eq. (12)

Gas (A1)	S	Parameter	Temperature, K					
			278.15	283.15	288.15	298.15	308.15	318.15
Ar	**I**	$-K_s^0 \times 10^3$		286±3	244±2	165±3	89±3	26±5
		s_{A1A2}				8.74±0.18		
	II	$-K_s^0 \times 10^3$		295±1	256±2	178±2	105±3	42±5
		s_{A1A2}				8.42±0.12		
Kr	**I**	$-K_s^0 \times 10^3$	106±2		97±2	86±2	80±2	69±1
		s_{A1A2}				0.79±0.03		
	II	$-K_s^0 \times 10^3$	112±2		102±1	91±2	83±2	73±2
		s_{A1A2}				0.81±0.03		

The presence of urea in water fairly strongly affects the isotope effects in $\Delta_{solv}S^0_{Ar}$, which increase (become more positive) with increasing urea concentration. At the same time, variation of $c_{sm,A2}$ has virtually no effect on $\Delta_{solv}S^0_{Kr}$. Presumably, such a difference is due to the stronger interaction of krypton with the solvent [L + A2]. This is favored by increases in the molecular polarizability $\alpha_{0,A1}$ (by ~50%) and force constant of the Lennard–Jones 12–6 pair potential ε_{A1}/k (by ~30%) of the gas in going from Ar to Kr, despite the fact that the molecules (atoms) of these gases are comparable in size. For example, the hard sphere diameters σ_{Ar} and σ_{Kr} are 0.341 and 0.360 nm, respectively [5]. As a result, the molecules of $A2_{H(D)}$ and $L_{H(D)}$ participate in interaction with krypton molecules to equal extents. As shown in [2], the hydration complexes of urea and water clusters in the bulk of the solvent are complementary. However, probably, the hydration complexes of urea are not quite suited for interaction with argon atoms by the mechanism of hydrophobic hydration.

A very useful information about the interparticle interactions of the components of a ternary system forming on dissolution of a gas in a binary solvent can be derived from the concentration dependences of the Sechenov parameter K_s^0 describing how the solubility of one solute is influenced by the other solute. A detailed procedure for finding K_s^0 is given elsewhere [23]; here we give only the main thermodynamic relationships.

According to [23], the Gibbs energy of transfer of 1 mol of A1 from the standard {a hypothetical solution of unit concentration with the properties of an infinitely dilute (ideal) solution [24]} solution in a pure solvent L to the standard (with respect to A1) solution in [L + A2] at low $c_{sm,A2}$ can be expressed as follows:

$$\Delta_{tr}G^0_{A1}(L \rightarrow L + A2) = -RTK_s^0 c_{sm,A2} = -RTB_1 c_{sm,A2}, \quad (8)$$

where B_1 is the coefficient of the regression equation

$$\ln c_{sm,A1} - \ln c^*_{sm,A1} = B_1 c_{sm,A2} + B_2(c_{sm,A2})^2. \quad (9)$$

The numerical values of K_s^0 ($\equiv B_1$) for all the systems studied in this work are listed in Table 3.

On the other hand, the parameter $\Delta_{tr}G_{A1}$, according to the MacMillan–Meyer theory [25, 26], can be expanded in a power series in $c_{sm,A2}$. As applied to the conditions of the standard state, when the higher terms of the expansion tend to zero, the following relationship is valid:

$$\Delta_{tr}G^0_{A1} = 2c_{sm,A1}g_{A1A2}, \quad (10)$$

where g_{A1A2} is the parameter (of the Gibbs free energy) of pair interaction between solute particles.

If the concentration dependence of the solubility data (Table 1) is approximated by model (9), then from Eqs. (8) and (10) we obtain a formula for calculating g_{A1A2}:

$$g_{A1A2} = -RTB_1(\equiv K_s^0)/2. \quad (11)$$

The entropy s_{A1A2} (Ts_{A1A2}) and enthalpy h_{A1A2} coefficients of intermolecular interaction A1–A2 can be readily calculated by the known thermodynamic relationships based on approximation of the temperature dependence of g_{A1A2}:

$$g_{A1A2} = \sum_{j=0}^{2} \omega_j (T - 298.15)^j. \quad (12)$$

The coefficients ω_1 ($\equiv s_{A1A2}$) of empirical equation (12) are listed in Table 3, and the parameters

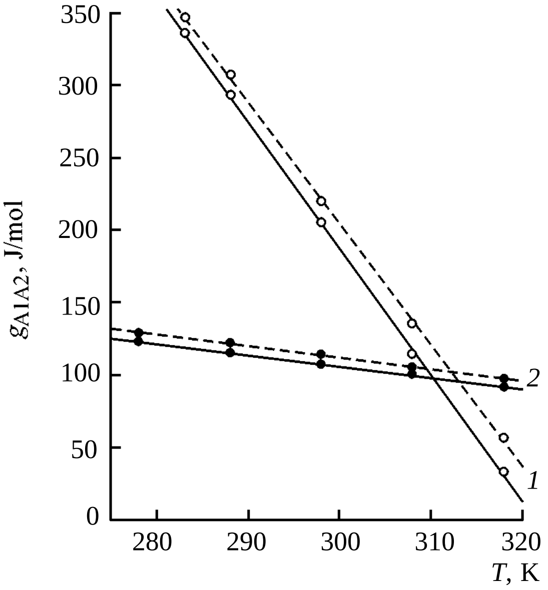

Fig. 2. Coefficients g_{A1A2} of pair interaction of (*1*) Ar and (*2*) Kr with (solid line) $CO(NH_2)_2$ in H_2O and (dashed line) $CO(ND_2)_2$ in D_2O, as functions of temperature T.

g_{A1A2} are plotted in Fig. 2.

The parameters f_{A1A2} ($f = g, h, s$) are contributions to the corresponding thermodynamic functions F ($\equiv G$, H, S), related to mutual approach of solvated A1 and A2 molecules from an infinitely large distance to a certain critical distance. Therefore, the parameters f_{A1A2} take into account new sources of nonideality in the ternary system, originating from weakening of the L–A1 and L–A2 interactions under the influence of the arising A1–A2 interactions.

Considering our results from this standpoint, we can state that the positive sign of g_{A1A2} in the entire temperature range studied (Fig. 2) suggests prevalence of mutual repulsion between the hydrated A1 atoms and A2 molecules. As a result, transfer of A1 from aqueous [$L_{H(D)}$] solution to a solution in [$L_{H(D)}$ + $A2_{H(D)}$] becomes thermodynamically unfavorable. With increasing temperature, g_{A1A2} decreases. Replacement of the protium solvent [L + A2] by its deuterium analog increases g_{A1A2}, i.e., the decrease in the solubility of A1 under the influence of A2 is more pronounced in the deuterated solvent system.

Comparison of the dependences $g_{A1A2} = f(T)$ (Fig. 2) and numerical values of s_{A1A2} (Table 3) for solutions of Ar and Kr shows that the system [$L_{H(D)}$ + + $A2_{H(D)}$ + Kr] has certain specific features as compared to the similar system with Ar.

For A1 = Ar, the coefficients g_{A1A2} sharply decrease with increasing temperature and become close to zero in the range 320–330 K, which suggests that in this temperature range the water–urea structural complexes interact with Ar similarly to the structural units of straight water.

The entropy coefficients s_{A1A2} (A1 = Ar) are positive and relatively large. According to the commonly used simplified concept, using quasigeometric analogies, the sign of the entropy characteristics is associated with changes in the ordering of the system or in the packing density of particles comprising the system.

It is more profitable to interpret s_{A1A2} using Gurney's concept [25] of overlap of the hydration cospheres of the interacting particles and the structural salting-in–salting-out concept based on it. According to this concept, the pair interaction of particles hydrated by different mechanisms (hydrophilic and hydrophobic in our case) leads to their mutual repulsion and increase in the fraction of water with a more distorted structure than in the bulk.

Interaction of hydrated molecules of Kr and $A2_{H(D)}$ is characterized by a weak influence of temperature on g_{A1A2} and, as a consequence, by a considerably (by a factor of ~10) lower s_{A1A2} compared to the system with Ar. The isotope effect in g_{A1A2} (A1 = Kr) is as small as ~7 J/mol, being virtually independent of temperature, and in s_{A1A2} it is close to zero. This fact probably reflects the above-discussed specific features of krypton solutions, primarily the capability of krypton atoms for van der Waals interaction with urea molecules, compensating to a significant extent the structural repulsion.

Thus, our results allow an important, in our opinion, conlcusion: As the molecular weight of noble gas is increased, more kinds of intermolecular interactions become operative, and these interactions become correlated to a greater extent.

EXPERIMENTAL

In the experiments we used ultrapure Ar and Kr (main substance content 99.996 and 99.9978 mol %, respectively). Water with natural isotopic abundance was deionized and then twice distilled in a Pyrex apparatus (the first distillation was performed from $KMnO_4$). The specific electrical conductivity of the purified water was 1.3–2 μS cm^{-1}. Heavy water D_2O (deuterium content 99.84 ± 0.01 at. %) had the specific electrical conductivity of ~1 μS cm^{-1}. Urea $(H_2N)_2CO$ was of ultrapure grade. Deuterourea $(D_2N)_2CO$ (deuterium content 99.0 ± 0.1 at. %, nitrogen content 43.7 wt %) was purchased from Izotop. Ureas were

Table 4. Bunsen absorption coefficients β_{A1} (cm^3 A1/dm^3 L$_{H(D)}$) of Ar and Kr in H/D isotopomers of water[a]

T, K	L$_H$–Ar	L$_D$–Ar	L$_H$–Kr	L$_D$–Kr
278.150	47.27, 47.12 [12]	53.58	**93.65**, 93.66, 93.65 [12], 93.727 [15]	**102.48**, 102.48
278.163	47.205 [13]			
283.150	41.91, 41.88 [12], 41.80 [32], 42.00 [13]	46.62, 46.73 [12], 46.49 [20]	80.87	87.99
283.157	42.023 [13]			
283.220	**41.86**, 41.85	**46.51**, 46.54		
288.150	37.61	41.14, 41.21 [20]	**70.64**, 70.67, 70.61 [12], 70.704 [15]	**76.57**, 76.54, 76.57 [20], 76.47 [19]
288.165	37.699 [13]			
288.170	**37.62**, 37.59	**41.10**, 41.12		
288.30		41.09 [5]		
293.150	34.11, 34.16 [32]	36.79, 36.69 [33]	62.48	67.41
298.150	**31.19**, 31.24, 31.258 [15], 31.21 [12], 31.406 [13]	**33.32**, 33.31	**55.81**, 55.84, 55.978 [15], 55.76 [12]	**60.16**, 60.07, 59.30 [20]
303.150	28.89, 28.87 [32]	30.51, 30.51 [33]	50.41	54.12
308.150	26.95, 26.912 [15]	28.25	**45.91**, 45.94, 46.052 [15], 45.86 [12]	**49.22**, 49.26, 49.20 [20]
308.159				49.21 [5]
308.250	**26.85**, 26.91	**28.23**, 28.21		
313.150	25.35	26.43, 26.40 [33]	42.25	45.28
318.150			**39.22**, 39.18, 39.13 [12]	**42.06**, 42.00, 41.98 [19]
318.170	**24.01**, 24.02, 24.099 [13]	**24.97**, 24.96		

[a] The quantities printed italic were calculated by Eq. (14), and those printed bold were determined in this work.

used without additional purification after vacuum drying for 48 h at 335 K and were stored in a vacuum desiccator over P_2O_5.

Urea solutions were prepared gravimetrically from degassed components in a dry evacuated box with an accuracy of ~1.0×10^{-4} c_{sm} units. The degassing procedure is described in detail in [27]. Samples were weighed on an analytical balance accurate to within 5×10^{-8} kg. The solubility was measured at a gas partial pressure of 101 325 Pa by the saturation procedure on a precision microgasometric unit described in detail in [28], with some modifications [29]. All the aspects of measurements are described in detail in [28, 29].

We expressed the solubility of A1 in the solvent L(+A2) in terms of the Bunsen absorption coefficients β_{A1}, which were calculated as follows:

$$\beta_{A1} = v_{A1}(T, p) \times 273.15 z_{A1}(\text{n.c.})/[v_L(T, p) T z_{A1}(T, p)]$$
$$= v_{A1}(\text{n.c.}) z_{A1}(\text{n.c.})/[v_L(T, p) z_{A1}(T, p)], \quad (13)$$

where $v_{A1}(T, p)$ and v_{A1}(n.c.) is the volume of the pure gas absorbed at the temperature T and referred, respectively, to the partial pressure $p_{A1} = p_{tot} =$ 101 325 Pa and to normal conditions (T 273.15 K, p_0 101 325 Pa); v_L is the volume of the degassed solvent (or solution) at T and p_{tot}; $z_{A1}(T, p)$ and z_{A1}(n.c.) are the comressibility coefficients of "real" gas A1. These quantities were calculated by the Lee–Kessler method [30]. It should be noted that, according to [7], the correction for nonideal behavior of a gas should be made when v_{A1} is measured with an accuracy better than 0.4%. In our experiments the solubility was measured accurate to ±0.3% for Ar and ±0.25 for Kr. Therefore, neglect of z_{A1} in formula (13) could lead to an additional error in determination of β_{A1} ($c_{sm,A1}$), reaching 0.5% (at worst, for the system [L$_H$ + A2$_H$ + Ar] at 318 K).

The accuracy of measuring β_{A1} was checked by data on solubility of oxygen in water (p 101 325 Pa), because data available for this gas are the most accurate and reliable [31].

Temperature, K	292.72	303.05	313.03
This work	30.97±0.06	26.34±0.07	23.28±0.06
Data of [31]	30.99	26.43	23.20

Also, to additionally check the reliability of our results, we combined our data with reliable published data on the solubility of Ar and Kr in pure H_2O and D_2O into samples common for each system (Table 4) and subjected these samples to least-squares treatment using the equation

$$\ln \beta_{A1} = q_0 + q_1 \times 100/T + q_2 \ln (T/100). \qquad (14)$$

Table 4 shows that our experiments give no significant fixed errors. Repeated measurements of β_{A1} at each temperature showed a good (within 0.2–0.3%) reproducibility. The random deviations did not exceed the errors in measurement of the solubility of Ar and Kr in H/D isotopomers of water.

All the molar quantities were calculated using the IUPAC table [34] of relative atomic weights: [A_r(H) 1.00794, A_r(D) 2.01416, A_r(O) 15.99994, A_r(N) 14.00674]. The molar volumes of gases, v^*_{Ar} 22 395 $cm^3\,mol^{-1}$ and v^*_{Kr} 22 388 $cm^3\,mol^{-1}$, were taken from [7].

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