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Solubility and Thermodynamics of Solvation of Krypton in Aqueous–Methanol Solutions of Urea at 101 325 Pa and 278–318 K:

I.[1] Effect of H/D Isotope Substitution

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Abstract—The solubility of Kr in H_2O–CD_3OH–$CO(NH_2)_2$ and D_2O–CH_3OD–$CO(ND_2)_2$ mixtures in the entire range of compositions of the mixed aqueous–methanol solvent at a urea content of up to 1.5 solvomolality units (mole fraction 0.0263) was measured at 101 325 Pa and 278.15–318.15 K (at 10 K step). The standard Sechenov parameters K_S^0 of the solubility of Kr and the thermodynamic parameters of krypton–urea pair interactions were determined. A differentiating effect of the H/D isotope substitution on K_S^0 was revealed: Upon deuteration of groups participating in strong hydrogen bonding, the Sechenov solubility parameter increases, and upon replacement of CH_3 by CD_3, decreases in the absolute value.

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In our previous paper [1] we analyzed the solubility and thermodynamic characteristics of solvation of Kr in the ternary system H_2O–MeOH–$CO(NH_2)_2$ and concluded that urea can be complementarily incorporated in the structure of the mixed aqueous–methanol solvent at an MeOH content of up to 50 mol %. At higher MeOH concentrations, the urea solvation shell becomes looser; as a result, the salting-out effect of urea on the Kr solubility becomes appreciably weaker.

To reveal possible causes of this effect of urea additions on the solubility of the noble gas in the water–methanol mixture and elucidate the role of hydrophilic and hydrophobic fragments of the alcohol molecule in the formation of H-bonded structures in the ternary system under consideration, we used the method of H/D isotope substitution [2]. As repeatedly noted previously [2–5], this method (in combination with other methods) furnishes the most complete information on structural transformations in liquid multicomponent systems with intermolecular hydrogen bonds and on mutual solvation of the system components.

In this paper we discuss the solubility of gaseous Kr in H_2O–CD_3OH–$CO(NH_2)_2$ and D_2O–CH_3OD–$CO(ND_2)_2$ mixtures. These systems were not studied previously. Hereinafter Kr is denoted as A1, and isotopomers of urea, water, and methanol, as A2, L1, and L2, respectively (the general designation for water–methanol mixtures L1–L2 is L).

The solubilities of Kr in the solvomolality units[2] $c_{sm,A1}$ are given in Table 1.

Comparison of the data given in [1] and in Table 1 shows that the deuteration of L1 and replacement of OH by OD in L2 cause the solubility of A1, on the whole, to increase, whereas the H/D substitution in the CH_3 group of the alcohol decreases the solubility of Kr in L, especially in alcohol-rich mixtures and at high temperatures. Additions of A2 weaken the effects of the isotope substitution in L2 and of temperature on the solubility of A1. However, to reveal reveal regular trends in the variation of the solubility of A1 under the action of A2 at deuterium substitution in components of the mixed solvent L(+A2), it is necessary to apply phenomenological approaches allowing detailed consideration of the observed changes (or H/D isotope effects) on the molecular level.

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

[2] The solvomolality $c_{sm,A}$ [2] is a dimensionless parameter of the solution composition expressing the concentration of component A: $c_{sm,A} = 55.50843n_A/n_L$, where n_A and n_L are the amounts of the solute and solvent L, respectively. The normalizing factor 55.50843 is numerically equal to the amount of H_2O (mol) in 1000 g of water.

Table 1. Solubility of Kr ($c_{sm,A1} \times 10^3$) in $H_2O–CD_3OH–CO(NH_2)_2$ and $D_2O–CH_3OD–CO(ND_2)_2$ mixtures at 101 325 Pa and 298.15–318.15 K[a]

$c_{sm,A2}$	T, K	Composition of aqueous–methanol solvent, x_{L2}					
		0	0.06	0.1	0.3	0.6	1.0[b]
		$H_2O–CD_3OH–CO(NH_2)_2$ system					
0[c]	278.15	4.183	4.848	4.934	6.999	20.27	61.47
	288.15	3.158	3.781	4.017	6.445	19.53	57.72
	298.15	2.500	3.095	3.425	6.070	18.90	54.31
	308.15	2.063	2.637	3.031	5.827	18.39	51.24
	318.15	1.769	2.334	2.777	5.689	17.96	48.50
1.5	278.15	3.702	4.325	4.570	6.858	19.89	59.34
	288.15	2.837	3.435	3.765	6.339	19.11	55.30
	298.15	2.280	2.856	3.243	5.984	18.44	51.62
	308.15	1.908	2.469	2.893	5.757	17.89	48.32
	318.15	1.659	2.212	2.666	5.630	17.42	45.39
		$D_2O–CD_3OD–CO(ND_2)_2$ system					
0	278.15	4.602	5.237	5.316	7.218	20.82	62.95
	288.15	3.438	4.044	4.281	6.621	20.05	59.13
	298.15	2.705	3.283	3.621	6.216	19.39	55.65
	318.15	2.218	2.783	3.186	5.956	18.84	52.50
	308.15	1.902	2.455	2.905	5.806	18.39	49.70
1.5	278.15	3.944	4.576	4.799	6.981	20.34	60.57
	288.15	3.003	3.602	3.917	6.436	19.51	56.41
	298.15	2.406	2.978	3.354	6.066	18.80	52.63
	308.15	2.008	2.566	2.981	5.830	18.20	49.23
	318.15	1.750	2.295	2.743	5.698	17.70	46.21

[a] $x_{A1} = c_{sm,A1}/(55.50843 + c_{sm,A1})$. To calculate K_S^0, we also used the data on the Kr solubility at $c_{sm,A2}$ 0.1, 0.2, 0.5, and 1.0. [b] Data of [6]. [c] Data of [1].

From this standpoint, the standard Sechenov solubility parameters K_S^0 characterizing variation of the solubility of a component under the influence of another component are an important source of information on the interparticle interaction in the system. A procedure for determining K_S^0 is described in detail in [1, 7]. The values of K_S^0 are given in Table 2; their comparison with the data for the nondeuterated system [1] shows that, upon deuteration of groups participating in strong hydrogen bonds, K_S^0 increases in the absolute value, whereas upon replacement of CH_3 by CD_3 it decreases. In other words, the H/D substitution exerts a differentiating effect on the Sechenov solubility parameter.

According to [8, 9], K_S^0 is related to the standard Gibbs energy $\Delta_{tr}G^0(A1, L \to L + A2)$ 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 amount of components of L remaining the same) and to the Gibbs parameter g_{A1A2} of the pair interaction of the solvated species A1 and A2 by

$$-RTK_s^0 c_{sm,A2} = \Delta_{tr}G^0(A1, L \to L + A2) = 2c_{sm,A2}g_{A1A2}.$$

The parameters g_{A1A2} and the enthalpy (h_{A1A2}) and entropy (s_{A1A2}, Ts_{A1A2}) coefficients of the pair interaction A1–A2, calculated from the temperature dependences of g_{A1A2}, are listed in Table 3.

Table 3 shows that the Gibbs parameter g_{A1A2} is positive in the entire composition range of the systems. That is, additions of urea thermodynamically hinder (an effect similar to salting-out) the transfer of 1 mol of Kr from L to L–A2, because of the mutual repulsion of solvated A1 atoms and A2 molecules. The deuteration of the CH_3 group in methanol does not noticeably affect g_{A1A2}, but the –OH/–OD substitution makes g_{A1A2} more positive compared to the nondeuterated mixture [1].

This is apparently associated with the fact that, as the D bonds formed by deuterourea with deuterated water and alcohol are stronger than H bonds, the solvation shells formed around the deuterourea molecules have the more stable structure. In this case, the effect

Table 2. Standard values of the Sechenov parameter ($-K_S^0 \times 10^3$) of the Kr solubility in H/D-isotopically substituted water–methanol–urea mixtures

T, K	Composition of aqueous–methanol solvent, x_{L2}					
	0	0.06	0.1	0.3	0.6	1.0
	$H_2O–CD_3OH–CO(NH_2)_2$ system					
278.15	111.3 ± 0.7	100.1 ± 0.5	78.9 ± 0.3	28.7 ± 0.2	25.1 ± 0.7	32.1 ± 0.4
288.15	101.3 ± 0.3	87.7 ± 0.7	72.2 ± 0.8	26.6 ± 0.5	26.8 ± 0.6	37.2 ± 0.5
298.15	90.7 ± 0.5	76.8 ± 0.4	63.4 ± 0.4	24.4 ± 0.4	29.3 ± 1.5	42.7 ± 0.4
308.15	81.9 ± 0.8	66.1 ± 0.6	57.8 ± 0.7	22.7 ± 0.4	31.2 ± 1.4	48.2 ± 0.6
318.15	72.9 ± 1.3	58.8 ± 1.0	52.7 ± 1.0	21.2 ± 0.5	31.8 ± 0.8	53.7 ± 0.5
	$D_2O–CH_3OD–CO(ND_2)_2$ system					
278.15	118.0 ± 0.9	109.1 ± 0.4	87.9 ± 0.2	37.5 ± 0.5	30.0 ± 0.8	34.7 ± 0.4
288.15	106.6 ± 1.1	95.1 ± 0.8	79.2 ± 1.3	34.2 ± 0.6	31.7 ± 0.5	40.3 ± 0.5
298.15	95.3 ± 1.3	82.9 ± 0.7	69.5 ± 0.9	31.0 ± 1.0	33.8 ± 1.1	46.4 ± 0.5
308.15	84.2 ± 0.8	71.5 ± 1.1	62.7 ± 0.8	28.3 ± 0.6	36.3 ± 0.8	51.2 ± 0.4
318.15	74.6 ± 1.0	61.8 ± 0.4	56.3 ± 0.5	26.6 ± 0.7	38.3 ± 1.2	58.0 ± 0.7

Table 3. Thermodynamic parameters of pair interaction A1–A2 in H/D-isotopically substituted water–methanol–krypton–urea mixtures 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}
	$H_2O–CD_3OH–CO(NH_2)_2$ system			
0	113 (0.2)	+0.81 (0.02)	+242	355 (5)
0.06	95 (0.1)	+0.96 (0.03)	+286	381 (8)
0.1	79 (0.1)	+0.56 (0.03)	+167	246 (9)
0.3	30 (0.1)	+0.15 (0.01)	+45	75 (4)
0.6	36 (0.5)	–0.34 (0.02)	–104	–68 (5)
1.0	53 (0.1)	–0.85 (0.01)	–253	–200 (2)
	$D_2O–CH_3OD–CO(ND_2)_2$ system			
0	118 (0.4)	+0.95 (0.02)	+283	371 (5)
0.06	103 (0.2)	+1.11 (0.01)	+331	434 (3)
0.1	86 (0.3)	+0.69 (0.03)	+206	292 (9)
0.3	38 (0.3)	+0.21 (0.01)	+63	101 (2)
0.6	42 (0.3)	–0.41 (0.01)	–122	–80 (3)
1.0	58 (0.2)	–0.91 (0.02)	–271	–213 (6)

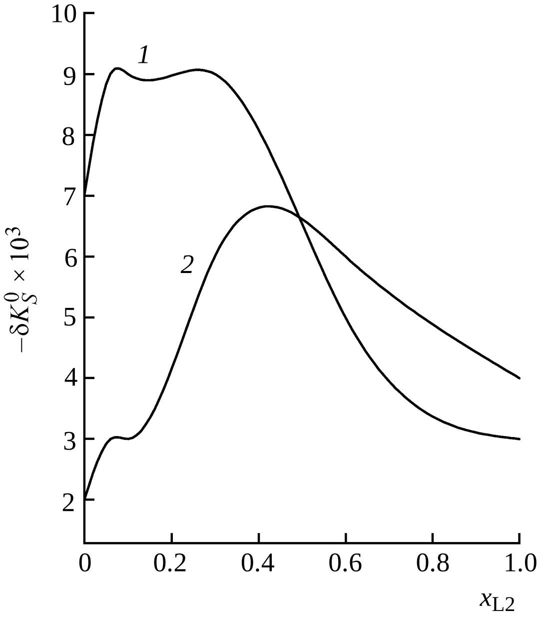
[a] In parentheses are standard deviations.

of “loosening” of the solvation shell of A2, discovered in [4] and manifested in that the molecules of A2 become more accessible to interaction with A1 atoms [4, 10] in going to alcohol-rich mixtures ($x_{L2} > 0.6$), becomes somewhat less pronounced.

Similar conclusions can be made from analysis of the isotope effects in the Sechenov coefficient (see figure) $\delta K_S^0(L_H \rightarrow L_D) = K_S^0(L_D) - K_S^0(L_H)$, where L_D and L_H are the solvents with the deuterated and nondeuterated (data from [1]) components, respectively.

The figure clearly demonstrates that the mechanism of solvation of A1 changes at x_{L2} ~0.3 (at 278 K) or ~0.5 (at 318 K). In the range $0 < x_{L2} < 0.3$ (0.5), the insertion mechanism involving hydrophobic stabilization of the structure of L1 with L2 molecules prevails, whereas at $x_{L2} > 0.3$ (0.5) the solvation (or substitution) mechanism becomes more and more prevailing [11].

We noted previously [5] that the promotion of the structure of L1 with A1 molecules is enhanced on



Isotope effect in the Sechenov solubility parameter as a function of the composition of the water–methanol mixture. Temperature, K: (*1*) 278.15 and (*2*) 318.15 (x_{L2} is the mole fraction of alcohol).

adding small (x_{L2} ~0.06) amounts of L2. As seen from the figure, this effect is manifested as a small maximum in the δK_S^0–x_{L2} dependences in this region of compositions. With an increase in temperature, this maximum becomes less pronounced because of the higher sensitivity of the D-bond networks in L1 and water–alcohol mixtures to external effects.

The results obtained allow two important conclusions. First, we revealed a nontrivial differentiating effect of the H/D isotope substitution on the Sechenov solubility parameter for a nonpolar gas: deuteration of groups forming strong intermolecular H bonds is accompanied by an increase in the absolute value of the negative parameters K_S^0, whereas the replacement of CH_3 by CD_3 in the methanol molecule, on the contrary, causes $|K_S^0|$ to decrease. The trends in variation of the isotope effect $\delta K_S^0(L_H \rightarrow L_D)$ with increasing temperature and alcohol content are indicative of the decisive role of specific interactions in the water–methanol–urea ternary system. Second, we confirmed the previously made (for the nondeuterated system) conclusion that the urea molecules can be complementarily incorporated into the structure of the isotopically substituted water–methanol mixture up to a methanol mole fraction of 0.3–0.5 (depending on temperature). This is indicated, in particular, by a change in the solvation mechanism (insertion → substitution) of the noble gas and an inversion of the sign of the isotope effects in the thermodynamic (entropy and enthalpy) parameters of the pair interaction between the solvated krypton atoms and urea molecules in this region of compositions.

EXPERIMENTAL

The quality parameters of krypton and water (natural isotope composition) were the same as in [1]. Heavy water D_2O (Izotop) with the conductivity æ ~1×10^{-5} S m^{-1} contained 99.83 ± 0.02 at. % D (densimetric monitoring). Deuteromethanols CD_3OH and CH_3OD (Izotop) containing 99.0 ± 0.1 at. % D (evaluated from the integral intensities of the IR absorption bands) were dehydrated with $Mg(OCH_3)_2$ [1] in a distillation installation under the conditions excluding the H/D isotope exchange [12]. The stability of the isotopic composition of the deuteroalcohols was checked by comparing the densities of the starting methanols (extrapolated to infinitely low moisture content) and purification products. Urea (ultrapure grade) and deuterourea $CO(ND_2)_2$ (Izotop, 99.0 ± 0.1 at. % D) were used without additional purification and, after drying for 48 h in a vacuum at 60°C, were stored in a vacuum desiccator over P_2O_5. All the manipulations with ureas and solvents were performed in a dry box.

Solutions were prepared gravimetrically from the degassed components in special evacuated mixers with an error not exceeding 1.0×10^{-4} $c_{sm,A2}$ unit. The Kr solubility was measured at a partial pressure $\bar{p}_{Kr}$ ~101 325 Pa by the saturation method on a precision microgasometric unit [13] with an error not exceeding 0.3%.

Treatment of the experimental data involved calculation of the equilibrium (corrected for nonideality) Bunsen absorption coefficients β_{A1} of gas A1 in solvent L and recalculation of β_{A1} to the solvomolality scale. The calculation procedure is described in detail in [1, 13]. The densities of the solutions in hand were reported in [4].

The molar weights of the deuterated compounds were calculated using the relative atomic weight of deuterium A_r(D) 2.01416 [14].

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