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Effect of H/D-isotope substitution on the solubility and solvation thermodynamics of krypton in methanol solutions of carbamide

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The solubility of gaseous krypton in $CO(NH_2)_2$—CH_3OH (CD_3OH) and $CO(ND_2)_2$—CH_3OD solutions with carbamide concentrations of up to 1.5 solvomolality units (~0.026 mole fractions) was measured at 278, 288, 298, 308, and 318 K and at a partial gas pressure of 101325 Pa. The thermodynamic functions of dissolution (solvation) of krypton and the standard Setchenov coefficients were calculated. The solvation of Kr molecules increases upon deuterium substitution and with an increase in the temperature and carbamide concentration. In these solutions, specific contacts between the carbamide and methanol molecules play the predominant role.

Key words: carbamide, krypton, methanol, solubility, isotope effects, solvation, thermodynamic functions.

Solutions of carbamide in methanol are of interest not less than carbamide—water mixtures. The replacement of the aqueous medium by methanol is accompanied by not only a considerable decrease in the endothermic effect of carbamide dissolution (4.8 kJ mol^{-1} from calorimetry data[1]) but also a decrease in the partial molar volume of $CO(NH_2)_2$ by up to 20%.[2—4] Yet another important feature of the methanol—carbamide system is that the partial molar volume ($\bar{V}_2^{\infty}$) decreases with an increase in temperature. This "negative expansion" of a dissolved (solvated) compound had been known previously only for infinitely dilute solutions of water in methanol[5,6] and *tert*-butyl alcohol.[7,8]

Useful information concerning the nature of solvation of a solute in methanol solutions of carbamide was obtained in our study[4] dealing with bulk properties of these solutions using H/D isotope substitution. The isotope effects in the bulk properties of the methanol—carbamide system are related to deuterium substitution both in the solvent and solute molecules; this complicates interpretation of the results.

This problem could be solved in part by investigating the solubility in this system of a noble gas that does not react chemically with the system components. This is due to specific features of solvation of noble gases related to the spherical symmetry and the relatively low polarizability of their atoms and also to low saturation concentrations of these compounds in methanol.[9] Due to the low solubility of the gas in the alcohol, structural macroeffects induced by the change in the interparticle interactions in the methanol—carbamide binary system under the influence of the indicator solute can be excluded from analysis of the thermodynamic functions of solvation.

In this work, we report the results of solubility measurements and calculations of standard thermodynamic functions for dissolution (solvation) of krypton (designated by A1) in solutions of carbamide $CO(NH_2)_2$ ($A2_H$) in methanol isotopomers, CH_3OH (L_H) and CD_3OH (L_{1D3}) and in a solution of deuteriocarbamide $CO(ND_2)_2$ ($A2_D$) in deuteriomethanol CH_3OD (L_{D1}). The measurements were carried out at temperatures of 278.15, 288.15, 298.15, 308.15, and 318.15 K for concentrations of carbamide ispotopomers equal to 0—1.5 solvolomolarity units c_{sm}*.

Experimental

Experimental procedure. The materials used in experiments included extra pure grade krypton with a content of the basic substance of at least 99.9978% (v/v), reagent grade methyl alcohol additionally purified by refluxing with magnesium methoxide and subsequent distillation to a purity degree of 0.99982 mole fractions (Fischer and densimetry analyses); deuterated methanols CD_3OH and CH_3OD (Izotop, Russia) with deuterium contents in the isotope-labeled positions of

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* Solvomolality $c_{sm,A}$ is a dimensionless parameter of the solution composition expressing the concentration of component A: $c_{sm,A} = (n_A/n_L)$ 55.50843, where n_A and n_L are the numbers of moles of the solute and the solvent,[10] and the normalizing factor 55.50843 is equal to the number of H_2O moles in 1000 g of water.

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99.0±0.1 at. % (based on the integral intensity of the absorption bands in the IR spectrum) and with a residual water content of at most $2 \cdot 10^{-4}$ mole fractions. The starting D isotopomers of methyl alcohol were dried by the procedure indicated for CH_3OH using the microapparatus that we have designed.[11] The preliminary evacuation of the setup followed by creation of an inert atmosphere above the reaction mixture ensured the absence of H/D isotope exchange during dehydration. The stability of the isotope composition of deuteriomethanols was checked by comparing the densities of the initial alcohols and of the products of their purification, which were extrapolated to an infinitesimal water content. All operations with alcohols and their storage were performed in a "dry box." Carbamide (extra pure grade) and deuteriocarbamide (Izotop) with a deuterium content of 99.0±0.1 at. % and a nitrogen content of 43.7% (w/w) were used. The carbamides were not subjected to additional purification; after drying for 48 h *in vacuo* at 335 K, they were stored in a vacuum desiccator over P_2O_5.

Solutions of carbamides were prepared by the weighing method using components preliminarily degasified by a known procedure,[12] in special evacuated mixers with an accuracy of at least $1.0 \cdot 10^{-4}$ $c_{\mathrm{sm,A2}}$ units. Weighing was carried out on an analytical balance with an error of at most $5 \cdot 10^{-5}$ g.

The solubility was measured at a krypton partial pressure of 101325 Pa by the saturation method using a precision microgasometric setup[13] with a ~10 cm^3 absorption vessel. The procedures of measurements were described previously.[13,14]

Processing of experimental results. The solubility of krypton was expressed as the equilibrium value of the Bunsen absorption coefficient (β) for gas A1 in solvent L(+A2)[10]

$$\beta_{\mathrm{A1}} = \nu_{\mathrm{A1}}(T,p)273.15z_{\mathrm{A1}}(\text{н.у.})/[\nu_{\mathrm{L}}(T,p)Tz_{\mathrm{A1}}(T,p)], \qquad (1)$$

where $\nu_{\mathrm{A1}}(T,p)$ is the volume of pure gas absorbed at the experiment temperature T and pressure p (equal to the partial pressure, p_{A1} = 101325 Pa); $\nu_{\mathrm{L}}(T,p)$ is the volume of the degased solvent or solution; $z_{\mathrm{A1}}(T,p)$ and $z_{\mathrm{A1}}(\mathrm{SC})$ are the compressibility factors for gaseous krypton at T, p and at standard conditions, respectively. The numerical values for the last-mentioned parameters were determined by the Lee—Kessler method.[15]

The accuracy of the measured β_{A1} values was estimated by comparing the determined solubility of O_2 in water with the most reliable published data.[16] Repeated measurements of the solubility of A1 in L_H demonstrated that the β_{A1} parameter is reproduced with an error of at most ±0.2%. Comparison of the $\beta(\mathrm{Kr,L_H})$ values that we obtained with the data published previously[18,19] (Table 1) shows insignificant (less than 0.4% at 278—308 K) divergence, because even for the H_2O—Kr system studied in detail, the scatter of the available[19,20] data on the limiting concentration of the second component exceeds 0.5%.

Table 1. Solubility of krypton in methanol ($\beta_{\mathrm{A1,LH}}$) at 101325 Pa

T/K	$\beta_{\mathrm{A1,LH}}$/cm^3 A1 dm^{-3} L_H		
	I[a]	II[b]	Our data
278.15	615.3	620.7	622.7
288.15	574.0	577.8	579.4
298.15	534.0	542.1	540.2
308.15	494.7	503.4	505.0
318.15	454.0	470.5	473.9

[a] See Ref. 17.

[b] See Ref. 18.

Table 2. Solubility of krypton ($c_{\mathrm{sm,A1}}$) in mixtures of methanol and carbamide H/D isotopomers at 101325 Pa and at different temperatures (278.15—318.15 K)*

Solvent	$c_{\mathrm{sm,A1}}$	$c_{\mathrm{sm,A1}} \cdot 10^3$				
		278.15	288.15	298.15	308.15	318.15
L_H—$A2_H$	0	61.44	57.84	54.57	51.65	49.06
	0.05	61.34	57.73	54.45	51.53	48.93
	0.1	61.24	57.62	54.33	51.40	48.80
	0.2	61.05	57.41	54.11	51.16	48.54
	0.5	60.52	56.83	53.47	50.47	47.82
	1.0	59.79	56.00	52.56	49.48	46.76
	1.5	59.25	55.35	51.81	48.65	45.87
L_{1D3}—$A2_H$	0	61.47	57.72	54.31	51.24	48.50
	0.05	61.37	57.61	54.19	51.12	48.37
	0.1	61.27	57.51	54.08	51.00	48.24
	0.2	61.09	57.31	53.86	50.76	47.99
	0.5	60.58	56.74	53.24	50.10	47.29
	1.0	59.87	55.93	52.35	49.12	46.26
	1.5	59.34	55.30	51.62	48.32	45.39
L_{D1}—$A2_D$	0	62.95	59.13	55.65	52.50	49.70
	0.05	62.84	59.01	55.52	52.36	49.56
	0.1	62.74	58.89	55.39	52.23	49.42
	0.2	62.53	58.67	55.15	51.97	49.14
	0.5	61.96	58.04	54.46	51.23	48.36
	1.0	61.17	57.13	53.45	50.14	47.19
	1.5	60.57	56.41	52.63	49.23	46.21

* If it is required to express the gas solubility and/or carbamide concentration in the scale of mole fractions, the relation $x_{\mathrm{A}} = c_{\mathrm{sm,A}}/(55.50843 + c_{\mathrm{sm,A}})$ should be used.

The results of measurements of krypton solubility in solutions of carbamide in methanol H/D isotopomers (Table 2) were expressed as solvomolality coefficients $c_{\mathrm{sm,A1}}$, which were determined by the equation[10]

$$c_{\mathrm{sm,A1}} = [\beta_{\mathrm{A1}}(55.50843M_{\mathrm{L}} + c_{\mathrm{sm,A2}}M_{\mathrm{A2}})]/(V^*_{\mathrm{A1}}\rho_{\mathrm{A2,L}}). \qquad (2)$$

Here M_{L} and M_{A2} are the molar weights of methanol (L_H, L_{1D3} or L_{D1}) and carbamide ($A2_H$ or $A2_D$), respectively, V^*_{A1} (22388 cm^3 mol^{-1})[21] is the real molar volume of krypton at the SC, $\rho_{\mathrm{A2,L}}$ is the density of a solution of A2 in solvent L. The data on the density of the studied solutions[4] are presented in Table 3 as coefficients of the regression equation

$$\rho_{\mathrm{A2,L}} - \rho^*_{\mathrm{L}}(\equiv a_0) = a_1c_{\mathrm{sm,A2}} + a_2(c_{\mathrm{sm,A2}})^2, \qquad (3)$$

where ρ^*_{L} is the density of pure methanol or its D isotopomer.

The solvomolality values were chosen for expressing the krypton solubility because they represent a convenient scale for the calculation of thermodynamic functions of dissolution (solvation) of a gas.[10,13] The thermodynamic parameters (Table 4) were calculated using[22] a physically justified mathematical model that described adequately the dependence of the solubility of the A1 substance, which does not chemically react with the medium

$$R\ln c_{\mathrm{sm,A1}} = b_0 + b_1u_1 + b_2u_2. \qquad (4)$$

Here $u_1 = (T - \theta)/T$, $u_2 = T/\theta + \ln(T/\theta) - 1$, where θ is a temperature chosen arbitrarily within the range of measure-

Table 3. Coefficients of Eq. (3)*

System	T/K	$a_0 \cdot 10^3$	$a_1 \cdot 10^4$	$-a_2 \cdot 10^4$
			g cm^{-3}	
L_H—$A2_H$	278.15	805.16	136.85(0.30)	4.12(0.23)
	288.15	795.79	137.98(0.17)	4.49(0.13)
	298.15	786.36	138.69(0.28)	4.50(0.21)
	308.15	776.88	140.00(0.15)	4.91(0.12)
	318.15	767.35	140.56(0.30)	4.68(0.23)
L_{1D3}—$A2_H$	278.15	885.10	123.79(0.20)	4.35(0.15)
	288.15	874.67	125.36(0.23)	4.79(0.18)
	298.15	864.20	126.95(0.23)	5.09(0.17)
	308.15	853.68	127.95(0.19)	5.04(0.15)
	318.15	843.11	129.50(0.29)	5.29(0.22)
L_{D1}—$A2_D$	278.15	828.93	150.05(0.26)	4.52(0.20)
	288.15	819.21	151.04(0.23)	4.66(0.18)
	298.15	809.46	151.87(0.24)	4.68(0.18)
	308.15	799.67	152.72(0.18)	4.85(0.14)
	318.15	789.83	153.64(0.21)	4.97(0.16)

* The standard deviations are indicated in parentheses.

ments. The b_i coefficients are not interdependent and, in physical meaning, they correspond to the standard molar thermodynamic functions of gas dissolution at the temperature θ: $b_0 = -\Delta_{sol}G_{A1}{}^{\varnothing}(\theta)/\theta$, $b_1 = \Delta_{sol}H_{A1}{}^{\infty}(\theta)/\theta$, $b_0 + b_1 = \Delta_{sol}S_{A1}{}^{\varnothing}(\theta)$, $b_2 = \Delta_{sol}c_{p,A1}{}^{\infty}$. The $\Delta_{sol}Y(\equiv H,c_p)_{A1}{}^{\infty}$ values were referred to infinite dilution according to the standardization conditions.

Table 4. Thermodynamic characteristics of krypton solvation in mixtures of methanol and carbamide H/D isotopomers at $c_{sm,A2}$ = 0 and 1.5 (the numbers in parentheses)

Solvent	T/K	$\Delta_{solv}G_{A1}{}^{\varnothing}$ [a]	$-\Delta_{solv}H_{A1}{}^{\infty}$	$-T\Delta_{solv}S_{A1}{}^{\varnothing}$
			kJ mol^{-1}	
L_H—$A2_H$	278.15	6.45	4.04±0.07	10.49±0.07
		(6.54)	(4.54±0.09)	(11.08±0.09)
	298.15 [b]	7.21	4.15±0.02	11.36±0.02
		(7.34)	(4.73±0.03)	(12.07±0.03)
	318.15	7.97	4.27±0.08	12.24±0.08
		(8.15)	(4.91±0.10)	(13.06±0.10)
L_{1D3}—$A2_H$	278.15	6.45	4.18±0.06	10.63±0.06
		(6.53)	(4.68±0.08)	(11.21±0.08)
	298.15 [c]	7.22	4.37±0.02	11.57±0.02
		(7.35)	(4.95±0.03)	(12.30±0.03)
	318.15	8.00	4.57±0.06	12.56±0.06
		(8.18)	(5.22±0.09)	(13.40±0.09)
L_{D1}—$A2_D$	278.15	6.40	4.15±0.07	10.55±0.07
		(6.48)	(4.71±0.07)	(11.19±0.07)
	298.15 [d]	7.16	4.36±0.02	11.52±0.02
		(7.30)	(5.00±0.02)	(12.30±0.03)
	318.15	7.94	4.57±0.08	12.51±0.08
		(8.13)	(5.29±0.08)	(13.42±0.08)

[a] The $\Delta_{solv}G_{A1}{}^{\varnothing}$ values were calculated with an error not exceeding ±7 J mol^{-1}.

[b] $-\Delta_{solv}c_{p,A1}{}^{\infty}$ = 6±3 (9±4) J mol^{-1} K^{-1}.

[c] $-\Delta_{solv}c_{p,A1}{}^{\infty}$ = 10±3 (14±4) J mol^{-1} K^{-1}.

[d] $-\Delta_{solv}c_{p,A1}{}^{\infty}$ = 11±3 (14±4) J mol^{-1} K^{-1}.

Results and Discussion

It can be seen from the data of Table 4 that the magnitudes of negative (by sign) enthalpy and entropy terms in the standard Gibbs energy of krypton solvation increase with an increase in temperature and carbamide concentration (L—A2). This tendency is more pronounced for the D isotopomers. The values of transfer functions (thermodynamic characteristics of the isotope effects of solvation), $\Delta_{tr}\Delta_{solv}Y(\equiv H^{\infty},S^{\varnothing})_{A1}(L_H \rightarrow L_D) = \Delta_{sol}Y_{A1}(L_D) - \Delta_{sol}Y_{A1}(L_H)$, virtually do not depend to within the error of calculations on what particular protium atom in the alcohol molecule has been replaced by deuterium, *i.e.*, the negative ($\Delta_{tr}c_{sm,A1}(L_H \rightarrow L_{1D3})$) and positive ($\Delta_{tr}c_{sm,A1}(L_H \rightarrow L_{D1})$) isotope effects in the gas solubility (see Table 2) are actually matched by the same $\Delta_{tr}\Delta_{solv}S_{A1}{}^{\varnothing}(L_H \rightarrow L_D)$ and $\Delta_{tr}\Delta_{solv}H_{A1}{}^{\infty}(L_H \rightarrow L_D)$ values (see Table 4).

According to the data obtained previously,[23,24] deuterium substitution in the methanol molecule decreases its size and its vibration energy. In the case of the $L_H \rightarrow L_{D1}$ substitution, this results in the formation of more extensive deuterium bonds and, as a consequence, in an increase in the free (or so-called "excluded") volume in the alcohol structure. Conversely, the $L_H \rightarrow L_{1D3}$ substitution gives rise to a more compact methanol structure despite the weakening of intermolecular H bonds.[24] However, this apparent contradiction can be understood by taking into account the increase in the energy of nonspecific interaction $\Delta_{tr}E_{nsp}(L_H \rightarrow L_{1D3}) \approx 0.1$ kJ mol^{-1}, found in our previous publication.[25]

These volume effects generally correspond to the observed (see Table 2) pattern of distribution of the $\Delta_{tr}c_{sm,A1}(L_H \rightarrow L_D)$ values; this suggests the predominant role of the configurational (geometrical) changes in the solvation shell of the A1 molecule caused by the replacement of protium by deuterium. The absence of the $\Delta_{tr}c_{sm,A1}(L_H \rightarrow L_{1D3})$ isotope effect at 278 K (see Table 2) is due most likely to the fact that the loss of some free space (configurational changes) in the structural matrix of the solvent is counterbalanced by the "vibrational" enhancement of the alcohol—gas interaction. According to published data,[26] this is predetermined by the possibility of orientation (from the standpoint of energy preferentiality) of the hydroxyl oxygen atom toward A1. At higher temperatures, the isotope difference between the zero-point vibration energies of the L_H and L_{1D3} methanol molecules decreases faster than the difference between the energies of hydrogen bonds.[23,26] This brings about an increasing (in magnitude) negative isotope effect in the krypton solubility (see Table 2).

An increase in the carbamide content in the methanol solution, like an increase in temperature, results in a lower solubility of the gas. This effect is more pronounced in the more structured L_{D1}—$A2_D$ system (see Table 2).

According to the results of a study[4] of the excess bulk properties of the $L_{H(D)}$—$A2_{H(D)}$ system, the decrease in the $c_{sm,A1}$ and $\Delta_{tr}c_{sm,A1}$ values (L_H—$A2_H \rightarrow L_{D1} + A2_D$) may be due to the formation of structures (solvation complexes), more compact than those in the alcohol bulk, involving the solute $A2_{H(D)}$ and solvent $L_{H(D)}$ molecules. The increase in the negative (by sign) entropy and enthalpy effects of gas solvation and the isotope effects corresponding to these characteristics (see Table 4) give grounds to believe that the formation of these solvation complexes enhances the alcohol—gas interaction, which shows itself to a larger extent in deuteriomethanols.

Unlike the L_{D1}—A1—$A2_D$ system, in the L_{1D3}—A1—$A2_H$ solution, an increase in the carbamide solution counteracts the decrease in the gas solubility upon a rise of the temperature. This is related not only to intensification of the universal (dispersion) interactions between the nonpolar groups of the alcohol and the solute atoms but also to weakening of the specific contacts both in the solvent bulk and in the newly formed carbamide—methanol solvation complexes.

Attention is drawn by the difference between the values of the $\Delta_{tr}\Delta_{solv}Y(\equiv H^{\infty},S^{\varnothing})_{A1}(L_H$—$A2_H \rightarrow L_{D1} + A2_D)$ transfer functions for neat methanol and a solution with $c_{sm,A2} = 1.5$, which is beyond the error of calculations (at least, at 298 K) (see Table 4). In the case of the ($L_H + A2_H \rightarrow L_{1D3} + A2_D$) substitution, the $\Delta_{tr}\Delta_{solv}S_{A1}{}^{\varnothing}$ and $\Delta_{tr}\Delta_{solv}H_{A1}{}^{\infty}$ values remain invariable over the whole range of concentrations and temperatures.

In our opinion and in the opinion of other researchers,[1] a possible reason for the increase (in magnitude) of the negative isotope effects in the thermodynamic characteristics of gas solvation following the addition of the $A2_D$ substance to the L_{D1}—A1 solution is the ability of the H atoms of the methanol hydroxy groups to form hydrogen bonds with the amino groups of the carbamide molecules due to the lone electron pairs of nitrogen. Another cause for this effect is the possibility of formation of weak C...O bonds between the carbonyl O atoms of dissolved carbamide and the methyl groups of the alcohol.

Useful information on the interparticle interactions between the components of the ternary system formed can be derived from analysis of the concentration curves for the standard values of the Setchenov parameter $K_S{}^{\varnothing}$, which characterizes the change in the solubility of one component under the influence of the other one. The procedure of estimation of the $K_S{}^{\varnothing}$ value has been described in detail previously.[27,28] It has been reported[27] that the change in the Gibbs energy upon the transfer of one mole of A1 from a standard solution in neat solvent L into a standard solution* with respect to the A1 state (L—A2) at low $c_{sm,A2}$ values is expressed as

Table 5. Standard values of the Setchenov coefficients ($K_S{}^{\varnothing}$) for krypton solubility in the methanol—carbamide system at various temperatures (278.15—318.15 K)

Solvent	$-K_S{}^{\varnothing} \cdot 10^3$				
	278.15	288.15	298.15	308.15	318.15
L_H—$A2_H$	33.2±0.3	38.3±0.3	43.7±0.5	49.1±0.5	54.4±0.3
L_{1D3}—$A2_H$	32.1±0.4	37.2±0.5	42.7±0.4	48.2±0.6	53.7±0.5
L_{D1}—$A2_D$	34.7±0.4	40.3±0.5	46.4±0.5	52.1±0.4	58.0±0.7

$$\Delta_{tr}G_{A1}{}^{\varnothing}(L \rightarrow L\text{—}A2) = -RTb_1(\equiv K_S{}^{\varnothing})c_{sm,A2}, \qquad (5)$$

where b_1 is a coefficient of the regression equation

$$\ln c_{sm,A1} - \ln c^*{}_{sm,A1} = b_1 c_{sm,A2} + b_2(c_{sm,A2}), \qquad (6)$$

in which $c^*{}_{sm,A1}$ is the gas solubility in the neat solvent L ($\equiv L_H$, L_{D1}, L_{1D3}).

It follows from analysis of the $K_S{}^{\varnothing}$ values (Table 5) that the effect of "salting-out" (ejection) of gas A1 from the solution under the influence of solute A2 becomes more pronounced with an increase in temperature and after the $L_H(A2_H) \rightarrow L_{D1}(A2_D)$ deuterium substitution.

However, taking into account conclusions from the McMillan—Maier theory as applied to the standard state of the system considered, the $\Delta G_{A1}{}^{\varnothing}$ value can be expressed using the equation[27]

$$\Delta G_{A1}{}^{\varnothing}(L \rightarrow L\text{—}A2) = 2c_{sm,A2}g_{A1A2}. \qquad (7)$$

Here g_{A1A2} has the meaning of a coefficient or parameter of the standard Gibbs energy of solvation that represents the interaction between the particles of the solutes.

If the concentration curve of the solubility (see Table 2) is approximated by a type (6) model, Eqs. (5) and (7) can be converted into the relation

$$g_{A1A2} = -RTb_1/2. \qquad (8)$$

The enthalpy (h_{A1A2}) and entropy (s_{A1A2}) coefficients are calculated using known thermodynamic relations based on approximation of the dependence of g_{A1A2} on T by the empirical equation

$$gA1A2 \sum_{j=0}^{2} e_j\,(T - 298.15)j. \qquad (9)$$

The y_{A1A2} coefficients ($y = g$, h, s) (Fig. 1, Table 6) represent the contributions to the corresponding thermodynamic functions Y (G, H, S), which are related to the decrease in the distance between the solvated A1 and A2 molecules from an infinitely large to some critical value. Correspondingly, the y_{A1A2} values ($y = g$, h, s) take into account new sources of nonideal character of

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* The term standard solution is used to mean a hypothetical solution of unit concentration with properties of an infinitely dilute (ideal) solution.[29]

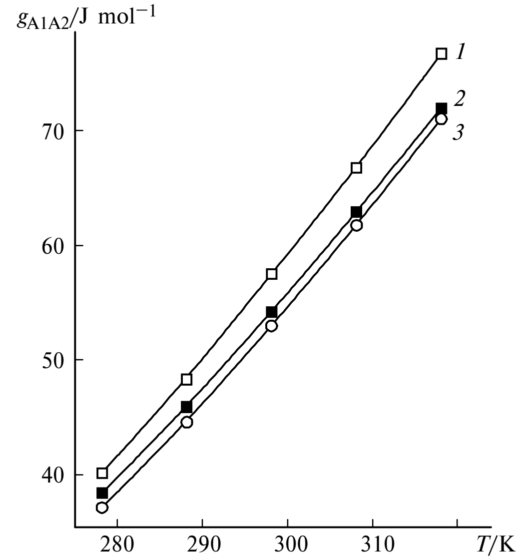

Fig. 1. Temperature dependences of the g_{A1A2} coefficients for solutions of carbamide isotopomers in L_{D1} (*1*), L_H (*2*), and L_{1D3} (*3*).

the ternary system, which arise due to the weakening of the L—A1 and L—A2 interactions under the influence of the newly formed A1—A2 contact.

When considering the obtained results from this standpoint, one can state that the g_{A1A2} values positive over the whole temperature range studied (see Fig. 1) point to repulsion between the solvated Kr atoms and carbamide isotopomer molecules. This entails thermodynamic hindrance to the transfer of gas A1 from methanol L (L_H, L_{D1}, L_{1D3}) to the solution ($L—A2_{H(D)}$). As the temperature rises, the g_{A1A2} values increase. The replacement of $L_H—A2_H$ by $L_D—A2_D$ also results in an increase in g_{A1A2}, *i.e.*, the decrease in the solubility of A1 in alcohol L_{D1} induced by the addition of $A2_D$ is enhanced. Thus, structural transformations are more pronounced in the L—A2 solvent associated through D bonds. The negative entropy coefficients s_{A1A2} (Table 6) imply that these transformations are related to an increase in the ordering of the system.

The relationship between the entropy parameters of the A1—A2 interaction $s_{A1A2}(L_{D1}) < s_{A1A2}(L_H) \approx s_{A1A2}(L_{1D3})$ (see Table 6) confirms the conclusion that the stabilizing action of the gas is manifested to a larger extent in the more structured (*i.e.*, having a greater electron-acceptor capacity of molecules) $L_{D1}—A2_D$ solvent. This is also consistent with the conclusion concerning the possibility of specific contacts between molecules L and the electron-donating centers of not only carbonyl groups but also the amino groups of A2. Thus it can be concluded that in the formation of the carbamide—methanol solvation complex, the key role is played by the O...O and N...O—H(D) intermolecular bonds. The contribution of universal (dispersion) interactions and the C...O bonds is less significant.

Table 6. Entropy and enthalpy coefficients y_{A1A2} ($\pm\Delta y_{A1A2} = 2\sigma$) at 298.15 K

System	$-s_{A1A2}$ /J mol^{-1} K^{-1}		h_{A1A2} /J mol^{-1}	
	$Kr—A2_{H(D)}$	$Ar—A2_H$[30]	$Kr—A2_{H(D)}$	$Ar—A2_H$[30]
$L_H—A1—A2_H$	0.84±0.03	0.81±0.07	195±7	175±20
$L_{1D3}—A1—A2_H$	0.85±0.03	—	200±7	—
$L_{D1}—A1—A2_D$	0.92±0.03	—	215±7	—

A similar conclusion can be drawn by comparing the $K_S^{\varnothing} = f(T)$ dependences for solutions of Ar and Kr in $L_H—A2_H$ (Fig. 2). It can be seen that the decrease in the molecular polarizability $\alpha_{0,A1}$ upon the Kr → Ar replacement induces a more substantial decrease (by ~30%) in gas solubility (or an increase in g_{A1A2}) under the action of solvated $A2_H$ molecules. This reflects a specific feature of krypton solutions that shows itself as the capability of its atoms of being involved in dispersion interactions with carbamide molecules.

The data of Table 6 show that the s_{A1A2} parameters are approximately equal both for Ar or Kr in the $L_H—A2_H$ system and for Kr solutions upon the $L_H \rightarrow L_{1D3}$ substitution, which is also associated with the decrease in the molecular polarizability. However, unlike the former case (see Fig. 1), $g_{A1A2}(L_H) \approx g_{A1A2}(L_{1D3})$ (see Table 5), due to weakening of the specific interactions caused by a decrease in the proton-donating capacity of the $L_{1D3}—A2_H$ solvent.

In conclusion, we would like to note once again that the isotope substitution method can be used advantageously for the study of fine structural and solvation effects in solutions. In particular, the results obtained in this study convincingly demonstrate the incorrectness of

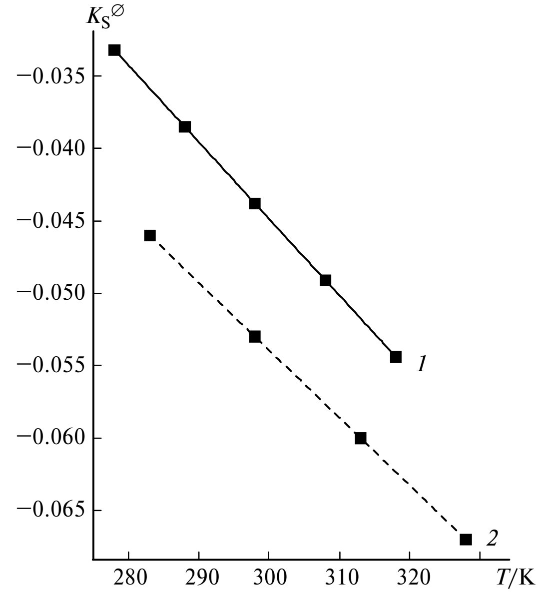

Fig. 2. Temperature dependences of the Setchenov parameters ($K_S^{\varnothing}$) for the solubility of krypton (*1*) and argon[30] (*2*) in $L_H—A2_H$ mixtures.

the opinion, frequently encountered in the literature, of the possibility of drawing analogies between water and methanol and clearly identify the structural features of methanol (as a solvent) and the solvation complexes it forms with carbamide.

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