Determination of thermodynamic functions of sorption for cyclohexyl-, piperidyl-, morpholyl-, and thiomorpholyl-*n*-alkanes by capillary gas-liquid chromatography

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The values of partial molar free energy (ΔG), enthalpy (ΔH), and entropy (ΔS) of sorption in the homologous series of *N*-alkylpiperidines, *N*-alkylmorpholines, *N*-alkylthiomorpholines, and alkylcyclohexanes were determined. It was found that the free energy of sorption is determined to a greater extent by the enthalpy term than by the entropy one. The free energy of sorption of the first homolog decreases when the *n*-alkyl chain is attached directly to the carbon atom of the cycle and increases in the case of *N*-alkylsubstituted heterocycles. The influence of the heteroatom nature on intermolecular interactions of homologs with the nonpolar stationary phase was quantitatively estimated on the basis of thermodynamic data.

Key words: capillary gas-liquid chromatography; *N*-alkyl-substituted piperidines, morpholines and thiomorpholines, cyclohexyl-*n*-alkanes; partial molar free energy, enthalpy and entropy of sorption.

N-Alkyl-substituted piperidines, morpholines, and thiomorpholines are physiologically active compounds, which requires that their presence in the environment be controlled. Quantitative thermodynamic parameters serve as the basis for the choice of optimum conditions of GLC analysis of organic compounds.

The purpose of this work is to determine thermodynamic functions (partial molar free energy, enthalpy and entropy of sorption) by capillary gas chromatography and to estimate the effect of the heteroatom nature on the thermodynamic parameters.

Experimental

The GLC analysis of the series of *N*-*n*-alkylpiperidines, *N*-*n*-alkylmorpholines, *N*-*n*-alkylthiomorpholines, and *n*-alkylcyclohexanes with the number of carbon atoms in the alkyl chain (m) equal to 5—6 was carried out on a Carlo Erba 5300 chromatograph of the Mega series with a flame-ionization detector on a glass capillary column with OV-101/KF (50 m×0.3 mm) with the film thickness of the stationary phase (d_f = 0.4 μm) prepared by a known method.[1] The temperature of an injector and a detector was 150—200 °C. The analysis was carried out under the isothermal conditions at 70, 90, 110, 130, and 150 °C. Helium was the carrier gas. The split ratio of the carrier gas flow at the inlet of the column was 1 : 30. The volume of a sample was 0.1 to 0.4 μL of 1—2 % solutions of homologs in pentane.

N-*n*-Alkyl-substituted nitrogen-containing heterocyclic bases were obtained as described previously,[2] and homologs of *n*-alkylcyclohexanes were synthesized by a known procedure.[3] The compounds studied are presented in Table 1.

Retention of compounds was characterized by the retention factor k'* (see Ref. 4). The partial molar free energy of sorption (ΔG) of homologs was calculated by the formula:

$$\Delta G^T = -2.3RT\log(k' \cdot \beta), \quad (1)$$

where T is the temperature of the analysis, K, and β is the phase ratio calculated by the formula[5]:

$$\beta = (d_c - 2d_f)^2/4(d_c d_f - d_f^2), \quad (2)$$

where d_c is the inner diameter of the capillary column and d_f is the film thickness of the stationary phase. For our column, β = 186.75. The partial molar entropy (ΔS) and enthalpy (ΔH) of sorption were determined from the equation

$$\Delta G = \Delta H - T\Delta S \quad (3)$$

after preliminary checking that the linear dependence of $\log k'$ on $1/T$ exists in the studied temperature range from 70 to 150 °C.

Results and Discussion

The resulting values of the partial molar free energy of sorption (ΔG), partial molar enthalpy (ΔH) and entropy (ΔS) of sorption for members of the homologous

* "Dead time" necessary for calculation of the retention factor was determined by the retention of methane injected into the column simultaneously with the sample.

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Table 1. Thermodynamic parameters of sorption of homologs of alkyl-substituted cyclic compounds in capillary gas chromatography

n-Alkyl	$-\Delta G^*$/kJ mol^{-1}				$-\Delta H$	$-\Delta S$
	70 °C	90 °C	110 °C	130 °C	/kJ mol^{-1}	/J mol^{-1} deg^{-1}
			n-Alkylcyclohexanes			
Methyl	13.17	12.21	11.33	10.51	28.33	44.30
Ethyl	15.54	14.57	13.45	12.59	32.63	49.85
Propyl	17.58	16.51	15.30	14.31	36.48	55.10
Butyl	19.72	18.54	17.19	16.13	40.50	60.60
Amyl	—	20.58	19.10	17.95	44.39	65.75
Hexyl	—	22.62	21.01	19.76	48.52	71.50
			N-*n*-Alkylpiperidines			
Methyl	13.88	13.00	12.09	11.15	29.50	45.50
Ethyl	15.67	14.69	13.70	12.68	32.76	49.80
Propyl	17.41	16.33	15.27	14.16	35.95	54.05
Butyl	19.46	18.26	17.12	15.91	39.68	58.95
Amyl	21.54	20.22	18.99	17.67	43.55	64.20
Hexyl	—	22.20	20.87	19.44	47.26	69.00
			N-*n*-Alkylmorpholines			
Methyl	14.36	13.35	12.40	11.54	30.46	47.05
Ethyl	16.32	15.21	14.16	13.15	34.41	52.80
Propyl	18.15	16.95	15.81	14.71	37.78	57.30
Butyl	20.24	18.93	17.68	16.49	41.65	62.50
Amyl	22.38	20.94	19.58	18.29	45.72	68.15
Hexyl	—	22.95	21.48	20.10	48.80	71.25
			N-*n*-Alkylthiomorpholines			
	90 °C	110 °C	130 °C	150 °C		
Methyl	16.80	15.84	14.91	13.97	34.44	48.45
Ethyl	18.63	17.48	16.47	15.53	37.35	51.70
Propyl	20.30	19.05	17.98	16.92	40.59	56.05
Butyl	22.25	20.89	19.73	18.55	44.45	61.30
Amyl	24.22	22.75	21.51	20.23	48.14	66.05

* Accuracy for determination of ΔG is ±0.04 kJ mol^{-1}.

series of *N*-*n*-alkylpiperidines, *N*-*n*-alkylmorpholines, *N*-alkylthiomorpholines, and *n*-alkylcyclohexanes (see Table 1) mainly reflect a change in energy of the dispersion interaction of the analyzed compounds with the nonpolar stationary phase. In all series, a usual tendency for a decrease in the free energy of sorption was observed as the temperature of the analysis increased. The comparative analysis of the dependences of the ΔG values on the length of the hydrocarbon chain (m) in the series studied made it possible to elucidate differences in the energy of sorption of compounds with the chair-like conformations of the cycles and by the existence and nature of heteroatoms, bond lengths in the cycles (C—C 1.54 Å, C—N 1.47 Å, C—O 1.43 Å, and C—S 1.82 Å), and values of angles in the cycles.[6,7] As can be seen from Fig. 1, in the case of the *n*-alkylcyclohexane series, the ΔG value for the first homolog (m = 1) deviates from the linear dependence, because the energy of interaction of methylcyclohexane with the stationary phase is lower than the ΔG value predicted from the linear dependence observed for the other members of this series. For *N*-substituted series, whose compounds contain the N atom directly attached to the *n*-alkyl substituent, the ΔG values for two former homologs (Me and Et) deviate to higher values compared to those following from the linear dependence (see dotted lines in Fig. 1). The presence of two heteroatoms in the cycle results in an increase in the deviation from the linear dependence of the free energy of sorption for the first homologs, as seen from the plots for morpholines and thiomorpholines. Thus, the presence of heteroatoms in the cycle results in an increase in the energy of dispersion interaction of the first homologs with the nonpolar phase compared to the energies of methyl- and ethylcyclohexanes. It is probable that conformational factors and their differences also affect the energy of interaction of cycles with the nonpolar phase.

The quantitative effect of the introduction of heteroatoms into the cycles and the substitution of the >CH—R_m bond for >N—R_m can be estimated from the $\delta(\Delta H)$ and $\delta(\Delta S)$ values in comparison of nitrogen-containing heterocycles with compounds of the cyclohexane series. As follows from Table 2, the heat of sorption increases by −1.17 kJ mol^{-1} when the CH_2 unit in the cycle is substituted by >NR. When the second O heteroatom is introduced into the piperidine cycle, $\delta(\Delta H)$ is −0.96 kJ mol^{-1}, although the molecular weight of the piperidine cycle differs from that of the morpholine cycle only by two units. The comparison of the differences in heats of sorption of methyl-substituted morpholine and thiomorpholine with that of piperidine shows that the introduction of the S atom instead of the

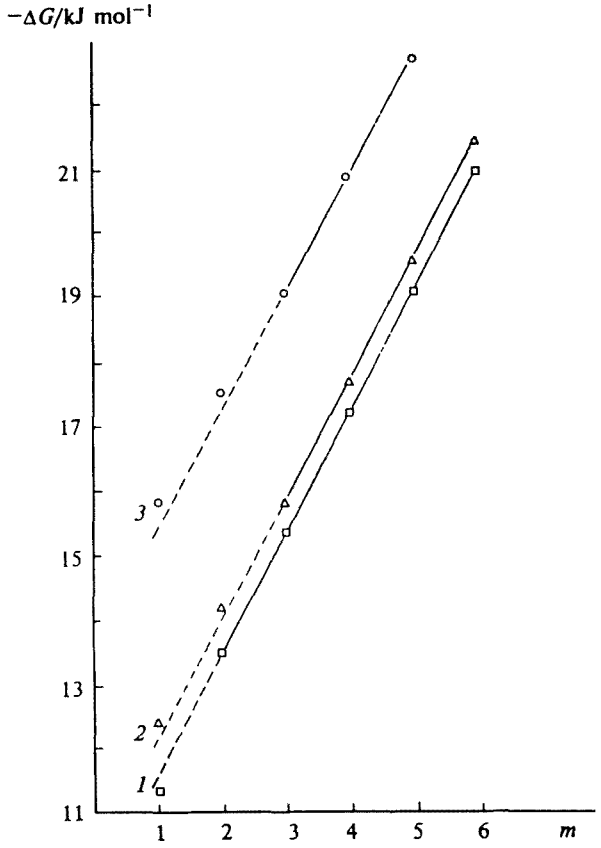
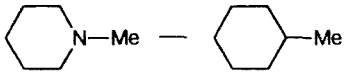
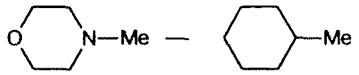
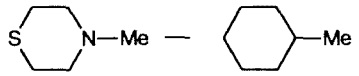
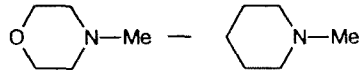
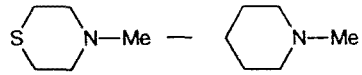
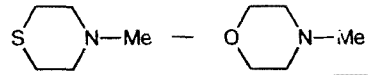


Fig. 1. Dependence of the partial molar free energy of sorption (ΔG) at 110 °C on the number of carbon atoms (m) in the n-alkyl chain in homologous series of alkylcyclohexane (*1*), N-alkylmorpholine (*2*), and N-alkylthiomorpholine (*3*). Dotted line shows the linear extrapolation.

O atom into the cycle results in a fivefold increase in $\delta(\Delta H)$, which makes it possible to estimate the effect of the heteroatom nature on the total energy of dispersion interaction with the phase. Perhaps, in the series of piperidines, morpholines, and thiomorpholines, the nonequivalence of bond lengths in cycles containing heteroatoms,[6,7] results in different surface areas of cycles and chair conformations capable of a greater number of contacts with the liquid phase. It affects the energy of dispersion interaction less than the nature of the heteroatom. Compared to methylpiperidine, the difference in the $\delta(\Delta S)$ value of methylthiomorpholine is two times higher than that of methylmorpholine, which is evidence for a lower degree of freedom of the molecule, and the $\delta(\Delta S)$ value is proportional to a change in the mass of heteroatoms. As a whole, the results of determination of the differences in thermodynamic values show that the nature of heteroatoms in the cycle exerts a stronger effect on a change in the heat of interaction with the phase and a weaker effect on a change in the degree of freedom of the molecule.

Table 2. Effect of the nature of heteroatoms on thermodynamic parameters of sorption of N-methyl-substituted heterocycles

Compared compounds	$-\delta\Delta H$ /kJ mol^{-1}	$-\delta\Delta S$ /J · mol^{-1} · deg^{-1}
	1.17	1.20
	2.13	2.75
	6.11	4.15
	0.96	1.55
	4.94	2.95
	3.98	1.40

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