pressure of 7-15 atm, flow rate 0.2-0.4 h^{-1}. The catalyzate was analyzed by GC on an LKhM-8MD chromatograph, catharometer detector, column length 2 m, packed with 15% PEG-2000 and 5% KOH on Chromosorb W (60-80 mesh). The column temperature was programmed from 50 to 220°C at a rate of 6°C/min. The carrier gas (helium) flow rate was 40 ml/min.

The pure products were isolated by vacuum fractionation of the catalyzate following separation of the aqueous layer and drying over potassium hydroxide. The physicochemical properties of the N-alkylfurfuryl- (I-IV) and N-alkyltetrahydrofurfurylamines (V-VIII) are given in Table 1. The properties of the N-alkylpiperidines (IX-XII) were in accordance with those given in [10]. ^{1}H PMR spectra were recorded on a BS-487C80 spectrometer (80 MHz) for 10% solutions in CCl$_4$, internal standard TMS. IR spectra were obtained on a UR-20 spectrometer.

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STRUCTURES AND PROPERTIES OF FURAN-2-CARBOXYLIC ACID ESTERS.

2.* THERMODYNAMICS OF SORPTION PROCESSES UNDER GLC CONDITIONS

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The interrelationship between the thermodynamic characteristics of the dissolving of furan-2-carboxylic acid esters in a nonpolar stationary liquid phase and the structures of the esters was investigated by GLC. Additivity of the contributions of the structural elements of 2-furoate molecules to the molar energy of dissolving was demonstrated. The existence of a compensating effect was noted, and the isokinetic temperatures of the process were calculated.

The use of GLC to study the physicochemical properties of organic compounds has undergone extensive development [2-4]; however, data on the use of this method in the investigation of furan-2-carboxylic acid esters are scanty and have analytical character in the overwhelming majority of cases [5-7].
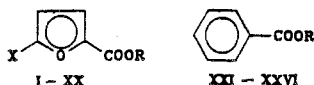
In a continuation of investigations of the physicochemical properties of 2-furoates and their interrelationship with their structures [8-10], in the present paper we present the

*See [1] for Communication 1.

TABLE 1. Thermodynamic Characteristics of the Retention of Furan-2-carboxylic and Benzoic Acid Esters on Apiezon

Compound	X	R	$V_{mm} \cdot 10^3$, moles SLP/moles gas	$\Delta F^0 \cdot 10^3$, kJ/mole	ΔH^0, kJ/mole	$\Delta S^0 \cdot 10^3$, kJ/mole-deg
I	H	CH_3	2,2	12,5	31,1	46,3
II	H	C_2H_5	81,3	14,7	39,8	62,2
III	H	C_3H_7	145	16,6	48,9	80,0
IV	H	C_4H_9	286	18,9	58,6	98,5
V	H	C_5H_{11}	435	20,4	65,5	112,0
VI	H	C_3H_5	143	16,6	50,0	83,0
VII	H	C_3H_3	139	16,6	53,8	92,5
VIII	H	CH_2—Fu*	833	22,6	60,3	93,6
IX	H	CH_2—Ph	3333	26,9	67,7	101,1
X	CH_3	C_3H_7	278	18,8	54,2	87,8
XI	CH_3	C_3H_5	263	18,7	54,2	88,2
XII	CH_3	C_3H_3	232	18,3	57,3	96,9
XIII	C_2H_5	C_3H_7	454	20,5	58,9	95,2
XIV	C_2H_5	C_3H_5	417	20,2	59,0	96,3
XV	C_2H_5	C_3H_3	454	20,5	60,9	100,1
XVI	Br	C_3H_7	625	21,5	59,4	93,9
XVII	Br	C_3H_5	588	21,4	60,0	95,7
XVIII	Br	C_3H_3	500	20,8	62,1	102,5
XIX	NO_2	C_3H_7	1111	23,3	64,3	101,6
XX	NO_2	C_3H_5	1429	24,4	66,8	105,2
XXI		CH_3	111	15,8	40,7	61,8
XXII		C_2H_5	204	17,8	49,5	78,7
XXIII		C_3H_7	370	19,8	57,1	92,5
XXIV		C_4H_9	667	21,8	65,3	107,9
XXV		C_3H_5	345	19,6	57,8	95,0
XXVI		C_3H_3	357	19,7	61,2	103,0

*SLF is the stationary liquid phase, Fu = 2-furyl.

the results of a study of the processes involved in the dissolving of furan-2-carboxylic acid esters in a nonpolar solvent under GLC conditions and attempt to correlate the thermodynamic characteristics of this process with the structures of the investigated compounds.

It is known that the functional relationship between the thermodynamic functions of the dissolving of sorbates in the stationary liquid phase during their gas-liquid chromatography and the experimentally·determined value of the polar retention volume V_{mm} lies at the foundation of the determination of these characteristics [2]:

$$\Delta F^0 = RT \ln V_{mm} = -RT \ln k_d = \Delta H^0 - T \Delta S^0,$$

where ΔF^0 is the free energy (kJ/mole), ΔH^0 is the free enthalpy (kJ/mole), ΔS^0 is the free entropy (kJ/mole-deg) for passing of the sorbate from solution into the gaseous state, and k_d is the coefficient of distribution of the sorbate between the liquid and gas phases.

In order to maximally decrease the effects of adsorption of the 2-furoates on the solvent—gas phase interface we used the low-polarity Apiezon L, which is a mixture of methyl phenyl ethers and hydrocarbons with an average molecular mass of 15,000, as the stationary liquid phase (solvent). Treatment of the solid support, Chromaton N "super," with hexamethyldisiloxane ensures the absence of adsorption of the esters on the stationary liquid phase—solid support interface, while coating it with Apiezon L in 15-17% amounts also ensures the absence of adsorption on the solid support—gas phase interface.

The experimentally found values of the molar thermodynamic functions of the dissolving of 2-furoates in Apiezon L are presented in Table 1. Data for a series of esters of benzoic acid are also presented in Table 1. From the data in Table 1 it may be concluded that relative molar free energy ΔF^0 increases with an increase in the molecular mass of the 2-furoates. The energies of retention of alkyl esters of benzoic and furan-2-carboxylic acids are approximated quite well by linear dependences on the number of atoms in the 2-furoates

$$(\Delta F^0 \pm 0.44) = (1.95 \pm 0.10) k_C + (10.7 \pm 1.2), \quad r = 0.996; \quad n = 14,$$

and benzoates

$$(\Delta F^0 \pm 0.28) = (1.98 \pm 0.13)k_C + (13.8 \pm 0.4), \quad r = 0.999; \quad n = 6.$$

The dependences obtained can be used for identification purposes and also serve as a confirmation of the primary contribution of dispersion forces to the retention energy [11, 12]. The deviations from a linear dependence are associated with an increase in the contribution of polar interaction to the total energy of the process.

Since Apiezon is a low-polarity phase, the fraction of orientation interaction of the solvent molecules with molecules of low-polarity esters will be extremely insignificant, and it can be disregarded with only a small error. The introduction into the ester molecules of multiple bonds then gives rise to a change in the anisotropic polarizability of the molecule [13] and, as a consequence, an increase in the molar enthalpy of the dissolving of allyl and propargyl 2-furoates as compared with propyl 2-furoate. The increase in the entropy of dissolving in the same series is evidently associated with an increase in the difference in the structures of the solvent molecules and molecules of the corresponding esters, although a 1.2 J/mole-deg decrease in the entropy was noted in [14] in the case of the presence of a terminal double bond in the olefin, which is explained by a decrease in the free energy of internal rotation. The contributions of the methylene groups that enter into the composition of the alkyl substituents in the 5 position of the furan ring and the alcohol part of the esters to the change in the molar enthalpies ΔH^0 and entropies ΔS^0 are different; the contribution is somewhat smaller in the first case than in the second case (Table 1, IV, V, and X-XIII). This effect may evidently be due to two factors that affect the change in the dispersion forces: interaction of the substituents in the 5 position of the heteroring with the electron system of the furan ring of the hyperconjugation type and a certain change in the geometry of the furan ring.

A halogen atom and a nitro group in the ring significantly increase the polarities of the 2-furoate molecules and change the geometrical structure of the ring [15], and the change in the parameters of dissolving of 2-furoates when these substituents are introduced into the second α position is therefore more complex and cannot be described by additivity rules.

Our attempt to correlate the ΔF^0, ΔH^0, and ΔS^0 values with the molecular refractions (MR_D) of the 2-furoates showed that linearity is observed only for saturated alkyl esters of furan-2-carboxylic acids (I-V; X, XIII). The corresponding equations have the form

$$(\Delta F^0 \pm 0.5) = (0.43 \pm 0.03)MR_D - (0.6 \pm 1.2) \quad (r = 0.998);$$

$$(\Delta H^0 \pm 2.3) = (1.9 \pm 0.2)MR_D - (27 \pm 6) \quad (r = 0.998);$$

$$(\Delta S^0 \pm 4.2) = (3.6 \pm 0.3)MR_D - (65 \pm 11) \quad (r = 0.999).$$

When substituents that have a characteristic group dipole moment are introduced into the 2-furoate molecules, the experimental points deviate from the experimentally found dependence in the direction of an increase in ΔF^0. This increase in the interaction energy may be due to contributions of orientation and atomic polarizabilities of the molecules of the sorbates. Taking into account the fact that the atomic polarizability does not exceed 10% of the electronic polarizability even for strongly polar compounds [16], its effect in this case can be disregarded, and the contribution of the orientation forces of intermolecular interaction can be evaluated as a certain fraction of the squares of the group dipole moments of the substituents [16], separately in the alcohol part and in the ring:

$$\Delta F^0 = (0.43 \pm 0.03)(MR_D + k_f \mu_{if}^2 + k_{al}\mu_{jal}^2) - (0.6 \pm 1.2), \qquad (1)$$

where μ_{if} and k_f are the group dipole moment of the substituent in the 5 position of the heteroring and the corresponding coefficient, and μ_{jal} and k_{al} are the group dipole moment of the substituent in the alcohol part of the 2-furoates and the corresponding coefficient.

Coefficients k_f and k_{al} can be found using model compounds (for example, propyl 2-furoates). For the investigated compounds $k_{al} = 3.2 \pm 0.2$ and $k_f = 1.1 \pm 0.1$. Substituting k_{al} and k_f into (1) we obtain

$$\Delta F^0 = (0.43 \pm 0.03)(MR_D + 3.2\mu_{jal}^2 + 1.1\mu_{if}^2) - (0.6 \pm 1.2).$$

This equation may serve as an illustration of the additivity of the energy of the dissolving of low-polarity compounds in nonpolar solvents under the conditions of infinitely dilute solutions:

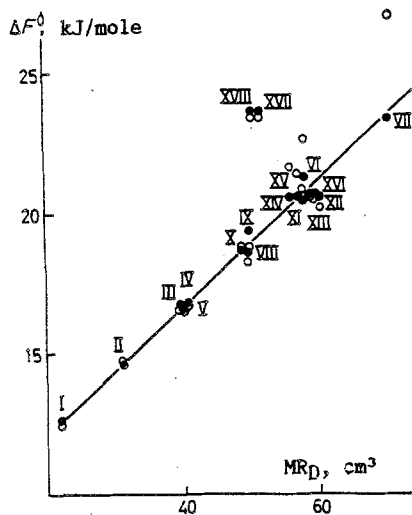$$\Delta F^0 = \Delta F^0_{disp} + \Delta F^0_{pol}$$

24

Fig. 1.

Fig. 2

Fig. 1. Dependence of the free molar energy of dissolving (ΔF^0) of furan-2-carboxylic acid esters in Apiezon L on their molecular refraction (MR_D) under GLC conditions: o) ΔF^0_{exp}; •) ΔF^0_{calc}.
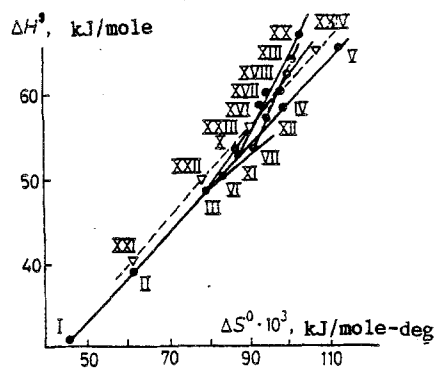
Fig. 2. Compensation effect in the dissolving of esters of furan-2-carboxylic (—•—) and benzoic (———∇———) acids in Apiezon L under GLC conditions.

The dependence of ΔF^0 on the volume and polarity of the sorbate molecules that we obtained makes it possible to determine the components of the energy of dissolving of 2-furoates in Apiezon L that are due to the introduction of various substituents into the furan ring and into the alcohol radical of the esters. The corresponding dependences $\Delta F^0 = f(MR_D)$ are presented in Fig. 1.

The substantial deviations of the theoretically calculated ΔF^0_{calc} values from the experimental ΔF^0_{exp} values are due either to steric factors or to additional disregarded intramolecular interactions such as the inductive effect, which are maximal when more polar or bulky substituents are present (VIII, IX, XVIII, XX).

Thus the equation that we obtained links in a most direct manner one of the indices of the solubility of the 2-furoates — the free molar energy of dissolving in a nonpolar solvent — with the structural parameters of the molecules.

On the basis of an analysis of the correlation dependences

$$\Delta H^0 = f(MR_D) \text{ and } \Delta S^0 = f(MR_D)$$

it may be concluded that the entropy factor makes the principal contribution to the free molar energy of dissolving of n-alkyl 2-furoates, since identical changes in MR_D give rise to greater changes in the entropy than in the enthalpy.

The effect of polar substituents in both the alcohol and acid parts of the esters on ΔH^0 and ΔS^0 is more complex and cannot be explained only by a change in the dipole moment of the molecules. For example, even methyl and ethyl groups, which have only a slight effect on the dipole moments of the molecules when they are introduced into the 5 position of the furan ring, give rise to a decrease in the free molar enthalpies and entropies of dissolving of saturated esters of furan-2-carboxylic acids as compared with esters that have the same numbers of methylene and methyl groups in the substituents (the same MR_D values) (for example, IV and X and V and XIII).

The existence of a linear relationship between the molar enthalpy and entropy of the process demonstrates the existence of a compensating effect, which was previously noted for some aliphatic compounds and alkylbenzenes [17], alkylphenols [18], and other compounds [19, 20] in GLC processes. Some authors define the compensating effect as a manifestation of the isokinetic or isoequilibrium dependence that is widely used in the study of the thermodynamics of solutions [17, 18, 21].

According to the empirical rule of Barclay and Butler, the ΔH^0 and ΔS^0 values for transition of a substance from the liquid phase to the gas phase exist in a linear dependence if strong interactions of the dipole-dipole type and the formation of hydrogen bonds, charge-transfer complexes, etc. are absent in the system [22].

Within the homologous series of saturated esters of furan-2-carboxylic acid the linear dependence

$$\Delta H^0 = \beta \Delta S^0 \qquad\qquad (2)$$

(β is the isokinetic temperature) is observed quite precisely, and the introduction of various substituents into the furan ring leads to scatter of the points around the overall line (Fig. 2). Only allyl and propargyl furan-2-carboxylates constitute an exception.

It is known that at the isokinetic temperature the differential energy of dissolving ΔF^0 does not depend on the structure of the substance being dissolved and that the sequence of the change in reactivity in this series changes to the opposite as this temperature is passed during the experiment [21]. Consequently, the isokinetic temperature can serve as one of the characteristics of the behavior of the investigated series of compounds in this process.

As we have already noted above, a single isokinetic dependence is absent in the dissolving of 2-furoates in Apiezon. Thus the following series of 2-furoates have individual isokinetic temperatures, which were determined as the slopes of linear dependences (2):

1. Unsubstituted 2-furoates with three carbon atoms in the alcohol radical (III, VI, VII), $\beta = 396 \pm 8$ K.

2. Unsubstituted 2-furoates with saturated paraffin alcohol radicals (I-V), $\beta = 525 \pm 3$ K.

3. 5-Substituted (in the ring) propyl 2-furoates (III, X, XIII, XVI, XIX), $\beta = 713 \pm 3$ K.

4. 5-Substituted (in the ring) allyl 2-furoates (VI, XI, XIV, XVII, XX), $\beta = 750 \pm 5$ K.

5. Ring-substituted propargyl 2-furoates (VII, XII, XV, XVIII), $\beta = 818 \pm 10$ K.

The isokinetic temperature for n-alkyl benzoates is somewhat higher than the isokinetic temperature for the corresponding series of n-alkyl 2-furoates: $\beta = 534 \pm 2$ K.

Attention is directed to the fact that the isokinetic dependence changes with a change in the polarity of substituents in both the alcohol and acid parts of the esters.

Since any isokinetic dependence is impossible when structural changes occur near the reaction center [21], it may be assumed that the polar intermolecular interactions that develop in the dissolving of 2-furoates in Apiezon L are realized over the entire structure of the ester molecues and not only over the ester group, as noted by Prokop'eva and Silkina [23]; analysis of the dependence of the change in the isokinetic temperature on the structures of furan-2-carboxylic acid esters demonstrates the considerably greater effect of substituents in the 5 position on the thermodynamic characteristics of dissolving than of substituents in the alcohol part of the esters.

Thus, as a result of these studies, we have demonstrated the additivity of the free molar energy of the dissolving of alkyl esters of furan-2-carboxylic acids in a nonpolar solvent under GLC conditions. At the same time, high polarizability of molecules of esters with a furan heteroring was noted. This effect was reflected in the inapplicability of the additivity principle to the thermodynamic components of the free molar energy of the process and in the absence of a single isokinetic dependence for the investigated esters. In addition, the quantitative data obtained, which characterize the intermolecular interactions of furan-containing compounds with a nonpolar solvent under conditions of infinitely dilute organic solutions, can be used for the further development of the theory of intermolecular interactions and the partition chromatography of complex molecules.

EXPERIMENTAL

The purity of the esters synthesized by the methods in [24] was no less than 99%.

The retention data were obtained with Soviet Tsvet-100 and Tsvet-102 chromatographs with a flame-ionization detector and stainless-steel columns with a length of 1 m and an inner diameter of 3 mm. For measuring and monitoring the pressure of the carrier gas (nitrogen) at the input into the column the chromatographs were additionally equipped with manometers of the 0.5 class for pressures up to 1.0 kgf/cm^2. The carrier-gas pressure at the input was 0.4 kgf/cm^2, whereas it was atmospheric pressure at the output. The space velocity of the carrier gas was measured with a foam flow meter and was maintained at 30 ± 0.3 cm^3/min. The recorder-chart speed was 600 mm/h. The substances to be analyzed were introduced into the vaporizer with a microsyringe of the MSh-1 type in 0.2-0.4 µl amounts; the solids were introduced in the form of solutions in acetone. The vaporizer temperature was 280-300°C, the temperature of the thermostat in the columns ranged from 80°C to 190°C at 10°C intervals, and the accuracy in maintaining the temperature in the thermostat was ±0.2°C.

The emergence time was determined from the maximum of the peak with an SD-51 two-hand stopwatch with 0.1-sec scale divisions. The amount of the stationary liquid phase in the column was determined from the total mass of the packing in the column and the amount of stationary liquid phase applied to the support.

The retention parameters (t_0 and t_R) were measured no less than six to seven times at five temperatures of the columns. The thermodynamic functions were calculated starting from the molar retention volume by the methods in [2].

All of the results obtained were treated by the method of least squares (P = 0.95). The errors in the determination of $\ln V_{mm}$, ΔH^0, and ΔS^0 did not exceed ±0.12, ±0.1 kJ/mole, and ±0.5 J/mole-deg, respectively.

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