ACTA UNIVERSITATIS LODZIENSIS
FOLIA CHIMICA 4, 1985

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ENTHALPY OF SOLUTION OF BENZOIC ALDEHYDE IN ALIPHATIC ALCOHOLS AT 298.15 K

Enthalpies of solution of benzoic aldehyde in methanol, ethanol, n-propanol, n-butanol, iso-butanol (2-methylpropanol-1), and butanol-2 were measured at 298.15 K in the range of concentrations from ca. 0.004 mole . kg^{-1} to ca. 0.04 mole . kg^{-1}. A linear correlation was found between the molal enthalpy of solutions of benzoic aldehyde in infinitely dilute solutions and Hancock's steric coefficients.

In recent years solutions of various kinds of organic compounds in polar and nonpolar solvents have been attracting a lot of attention of investigators. In the studies of solvation processes of considerable importance is the measurement of the enthalpies of solution, dilution and transfer [1 - 5]. The work conducted at our laboratory has included studies of the enthalpy of solution (ΔH_m) of benzoic acid and benzamide in aliphatic alcohols. The concentration dependences of the enthalpies of solution $\Delta H_m = f(m)$ for these compounds in the aliphatic alcohols studied have a linear character [6 - 9]. The straight lines obtained exhibit considerable slope in the case of all alcohols except methanol, whose solutions give lines parallel to the axis of concentrations. Studies of the solution enthalpies of methanol-benzoic acid media as well as of vapour elasticity and molal volumes indicate that these media behave like thermodynamically perfect solutions [6]. According to the authors of refs. [7 - 9] changes in the concentration dependence of the enthalpy of solution as well as differences in the first enthalpies of solution (ΔH_m^o) for benzoic acid and benzamide in the alcohols under investigation are due only to nonspecific interactions. By contrast with benzoic acid and benzamide, the enthalpies of solution of acetophenone and benzophenone in the aliphatic alcohols under

study [10] do not change in any distinct way with changes in the concentration. In view of the above, we thought it advisable to determine the enthalpy of solution of benzoic aldehyde in aliphatic alcohols as another representative of aromatic compounds which form associates with alcohols.

Experimental

Pure benzoic aldehyde supplied by POCh Gliwice Poland was distilled under reduced pressure. The fraction collected was the one which boiled at 338.4-338.9 K under the pressure of 12 mm Hg. Methyl alcohol p.a. and absolute ethyl alcohol were dried by the method of L u n d and B j e r r u m [11], while n-propyl, n-butyl and 2-methylpropanol-1 were dried with calcium hydride, and butanol-2 with calcium oxide, following which all alcohols were distilled. Enthalpies of solution were measured in a glass nonisothermal nonadiabatic calorimeter equipped with four high-resistance NTC type thermistors. The calorimeter had a capacity of about 300 cm^3. Using a V534 Meratronic digital voltmeter, changes in the voltage of unballanced Wheatstone bridge were determined and found to be a linear function of calorimeter temperature.

Results of measurements

The enthalpies of solution of benzoic aldehyde in the alcohols studies are collected in Tab. 1 and graphically represented in Fig. 1.

Discussion

The experimental results obtained indicate that concentration related changes in the enthalpy of solution of benzoic aldehyde in all alcohols are very small. The first enthalpy of solution ΔH_m^o was determined by the least squares method assuming a linear dependence of the enthalpy of solution ΔH_m in the range of con-

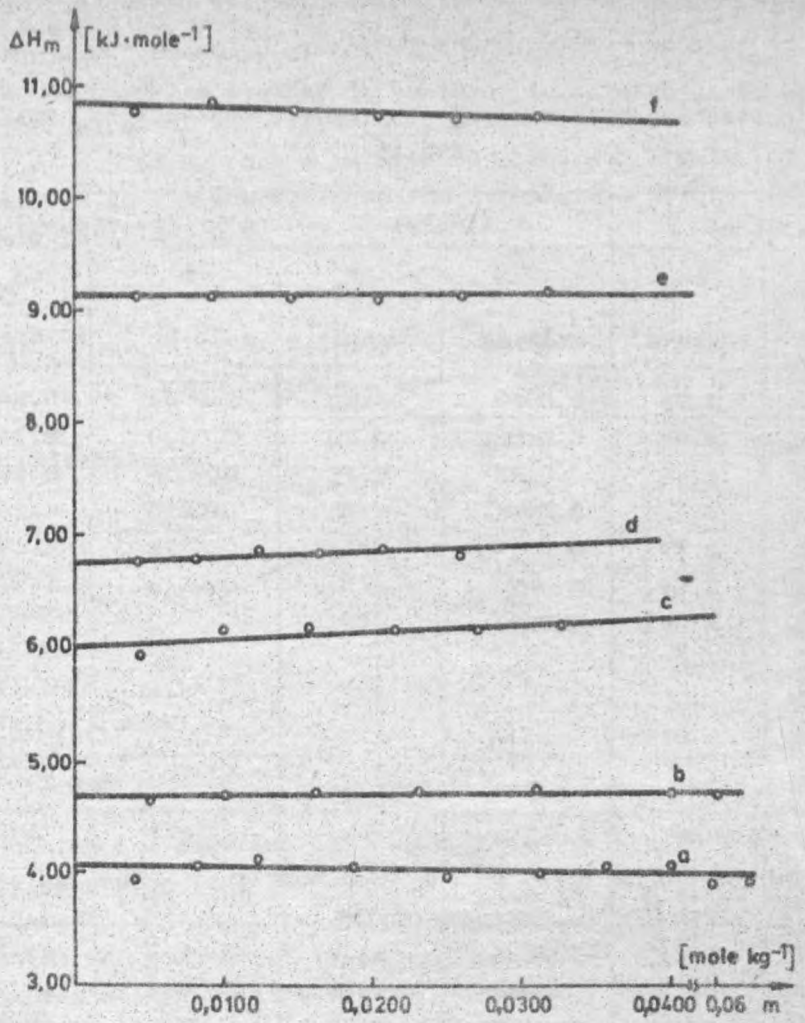

Fig. 1. The concentration dependence of the solution enthalpy (ΔH_m) of benzoic aldehyde in aliphatic alcohols at 298.15 K: a - methanol, b - ethanol, c - n-propanol, d - n-butanol, e - - 2-methyl-propanol-1, f - butanol-2

centrations under investigation $\Delta H_m = am + \Delta H_m^o$. In their monograph, Chapman and Shorter [12] cite examples of simples chemical reactions whoses enthalpies satisfy the equation of Taft. The authors of refs. [13] and [14] have also found a linear correlation to hold between the first enthalpies of solution ΔH_m^o of benzoic acid and benzamide and Hancock's

Table 1

Values of enthalpies of solution of benzoic aldehyde in the aliphatic alcohols studied (ΔH_m) and concentrations (m) at 298.15 K

methanol		ethanol		n-propanol	
m mole·kg^{-1}	ΔH_m kJ·mole^{-1}	m mole·kg^{-1}	ΔH_m kJ·mole^{-1}	m mole·kg^{-1}	ΔH_m kJ·mole^{-1}
0.0040	3.93	0.0050	4.63	0.0044	5.94
0.0082	4.07	0.0100	4.70	0.0100	6.15
0.0124	4.10	0.0163	4.72	0.0158	6.18
0.0188	4.04	0.0231	4.72	0.0215	6.14
0.0252	3.95	0.0310	4.74	0.0271	6.17
0.0313	3.99	0.409	4.72	0.0328	6.19
0.0356	4.06	0.0655	4.71		
0.0419	4.09				
0.0629	3.90				
0.0844	3.91				
n-butanol		2-methylpropanol-1		butanol-2	
m mole·kg^{-1}	ΔH_m kJ·mole^{-1}	m mole·kg^{-1}	ΔH_m kJ·mole^{-1}	m mole·kg^{-1}	ΔH_m kJ·mole^{-1}
0.0041	6.76	0.0041	9.14	0.0040	10.78
0.0080	6.79	0.0092	9.13	0.0092	10.86
0.0122	6.86	0.0146	9.12	0.0148	10.79
0.0164	6.85	0.0205	9.09	0.0204	10.72
0.0206	6.87	0.0262	9.13	0.0258	10.68
0.0259	6.80	0.0320	9.15	0.0312	10.70

steric coefficients for aliphatic alcohols substituents. In the present study a linear dependence was obtained between the values of the first enthalpies of solution of benzoic aldehyde and the values of Hancock's steric coefficients E_s^* for the alcohols under study:

$$\left(\Delta H_m^o\right)_{alc} = \delta E_s^* + \left(\Delta H_m^o\right)_{met}$$

where δ is steric susceptibility coefficient, and $(\Delta H_m^o)_{met}$ denotes the first enthalpy of solution of benzoic aldehyde in methyl alcohol.

The values of the first enthalpies of solution of benzoic aldehyde and of Hancock's steric coefficients are listed in Tab. 2 and the linear character of the correlation under discussion is depicted in Fig. 2.

Table 2

Values of the first enthalpies of solution of benzoic aldehyde (ΔH_m^o) and Hancock's steric. coefficients (E_s^*)

Alcohols	ΔH_m^o kJ . mole^{-1}	E_s^*
methanol	4.05	0
ethanol	4.68	-0.376
n-propanol	6.01	-0.666
n-butanol	6.76	-0.696
2-methylpropanol-1	9.13	-1.236
butanol-2	10.85	-1.632

During the solution of benzoic aldehyde in the alcohols under study an energetic effect takes place which is connected with the formation of hydrogen bonds between the molecules of benzoic aldehyde and alcohol. This is accompanied by energetic effects connected with the dissociation of a number of hydrogen bonds between alcohol molecules and with changes in nonspecific interactions.

The linear correlation between the values of standard enthalpy of solution (ΔH_m^o) and Hancock's steric coefficients (E_s^*) points to the absence of any significant induction effect of alcohol hydrocarbon radicals on the formation of hydrogen bonds and their dissociation. This may aslo indicate that the enthalpy of hydrogen bonds characterized by simple formation mechanism does not depend, or depends only very little, on the aliphatic alcohol hydrocarbon substituent, and changes in it are within experimental error. Furthermore, the linear character of the

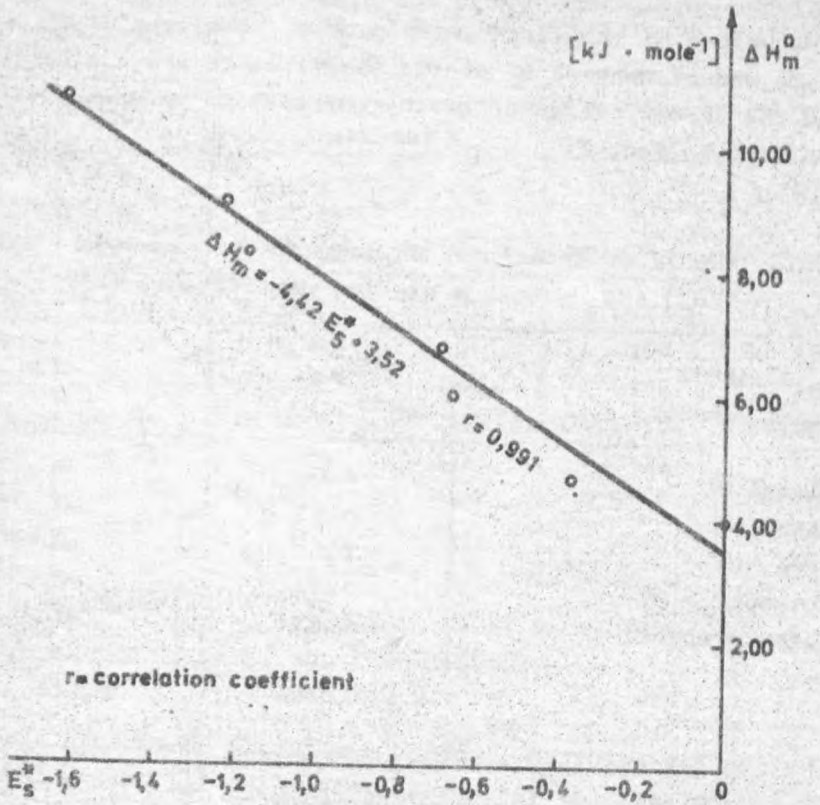

Fig. 2. Dependence of the standard enthalpies of benzoic aldehyde solution on Hancock's steric coefficients

function $\Delta H^{o}_{m} = f(E^{*}_{s})$ seems to suggest that in the alcohols under investigation associates of the same type arise between alcohol and benzoic aldehyde molecules with constant ratio of alcohol-aldehyde molecules in the associate.

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ENTALPIA ROZPUSZCZANIA ALDEHYDU BENZOESOWEGO W ALKOHOLACH ALIFATYCZNYCH W TEMPERATURZE 298.15 K

Zmierzono wartość entalpii rozpuszczania aldehydu benzoesowego w metanolu, etanolu, n-propanolu, n-butanolu, izo-butanolu (2-metylopropanolu-1), butanolu-2 w zakresie stężeń od około 0,004 mol . kg^{-1} do około 0.04 mol . kg^{-1} w temperaturze 298.15 K. Stwierdzono istnienie liniowej zależności pomiędzy molową

entalpię rozpuszczania aldehydu benzoesowego w roztworach o rozcieńczeniu nieskończenie dużym a współczynnikami sterycznymi Hancocka.

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ЭНТАЛЬПИЯ РАСТВОРЕНИЯ БЕНЗАЛЬДЕГИДА В АЛИФАТИЧЕСКИХ СПИРТАХ ПРИ ТЕМПЕРАТУРЕ 298.15 К

Измерена энтальпия растворения бензальдегида в метаноле, этаноле, н-пропаноле, н-бутаноле, изобутаноле (=2-метилпропаноле-1) и бутаноле-2 в пределах концентрации 0.004 мол.кг$^{-1}$ до 0.04 мол.кг$^{-1}$ при температуре 298.15 К. Оказалось что энтальпия растворения бензальдегида при бесконечном разбавлении является линейной функцией стерического коэффициента Ганкока.