ACTA UNIVERSITATIS LODZIENSIS
FOLIA CHIMICA 1, 1982

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THE MOLAL ENTHALPY OF SOLUTION OF ACETOPHENONE IN THE ALIPHATIC ALCOHOLS AT 286.16 K

The values of the enthalpy of solution of acetophenone in methanol, butanol-1, 2-methylpropanol-1 and butanol-2 within the concentration range from ca. 0.003 mole/kg to ca. 0.043 mole/kg at 286.16 K have been determined. It has been found that the heat of solution of acetophenone in the investigated alcohols is independent of concentration. The enthalpy of solution of acetophenone in the investigated alcohols at infinite dilutions has been obtained.

Much place in the literature has been devoted to the phenomenon of association of some substances in solutions. Benzoic acid solutions in the non-polar solvents belong to the most investigated ones. The concentration-dependence of the enthalpy of solution ΔH_m of benzoic acid in the non-polar solvents enables determination of the molal enthalpy of self-association [1-4].

The concentration-dependence of the enthalpy of solution of benzoic acid $\Delta H_m = f(m)$ in the aliphatic alcohols, unlike of its solutions in the non-polar solvents, is linear [5-7]. In the aliphatic alcohols benzoic acid forms mixed associates, probably of the AB_2 type (A - benzoic acid, B - alcohol) [5]. A similar course of the $\Delta H_m = f(m)$ function in the aliphatic alcohols has been observed with benzamide [7].

The results of the works cited above have stimulated me to investigate the enthalpy of solution of acetophenone in the aliphatic alcohols because unlike benzoic acid, acetophenone itself does not form associates, and the size of its molecules is similar to that of benzoic acid and benzamide molecules. To determine the concentration-dependence of the enthalpy of solution of the solid acetophenone in the investigated alcohols and eventually, to compare this dependence with the course of the $\Delta H_m = f(m)$ function for benzoic acid, the measurements of the heat of solution had to be made at 286.16 K in view of the fact that the melting point of acetophenone is 292.66 K.

Experimental

Pure acetophenone, obtained from USSR Reachim was distilled under vacuum. A fraction boiling within the temperature range from 84.5°C to 86°C at 14 mm Hg was collected. Methanol, analytical grade, was dried by the Lund-Bjerrum method [8], butanol-1, 2-methylpropanol-2 and butanol-2 were dried using calcium oxide and calcium hydride and then distilled in a high separating-power distillation column. The measurements of the solution heat were performed in a non-isothermic, non-adiabatic glass calorimeter. The calorimeter included NTC-type high-resistance thermistors. The volume of the calorimeter was ca. 300 m^3. Time-variations of the voltage in a Wheatstone bridge were measured using a digital voltmeter type V 534 Meratronik. Under the conditions of the measurement, the voltage variations proved to be a function of the calorimeter temperature. The precision of the calorimetry measurements was ±20 $cal \cdot mole^{-1}$ (1 cal = 4.184 J).

Results of the measurements

The measured values of the enthalpy of solution of acetophenone in the investigated alcohols are given in Table 1.

Because of the linear course of the realtion between the solution enthalpy and the concentration in the investigated alcohols, the first heat of solution ΔH_m^o was determined by graphical extrapolation.

Table 1

The values of the enthalpy of solution of acetophenone in the aliphatic alcohols at 286.16 K

Methanol		Butanol-1			
		serie 1		serie 2	
m	ΔH_m	m	ΔH_m	m	ΔH_m
mole·kg^{-1}	cal·mole^{-1}	mole·kg^{-1}	cal·mole^{-1}	mole·kg^{-1}	cal·mole^{-1}
0.0000	4625	0.0000	5450	0.0000	5428
0.0032	4619	0.0059	5448	0.0054	5434
0.0095	4625	0.0118	5450	0.0114	5422
0.0170	4627	0.0179	5462	0.0174	5429
0.0204	4622	0.0242	5450	0.0234	5423
0.0301	4620	0.0306	5452	0.0289	5411
0.0370	4625	0.0368	5448		
		0.0436	5440		
2-methylpropanol-1		Butanol-2			
		serie 1		serie 2	
m	ΔH_m	m	ΔH_m	m	ΔH_m
mole·kg^{-1}	cal·mole^{-1}	mole·kg^{-1}	cal·mole^{-1}	mole·kg^{-1}	cal·mole^{-1}
0.0000	6005	0.0000	6420	0.0000	6390
0.0058	6000	0.0053	6408	0.0061	6420
0.0129	5990	0.0113	6415	0.0128	6391
0.0196	6003	0.0180	6425	0.0175	6395
0.0254	6010	0.0241	6422	0.0226	6386
0.0323	6008	0.0306	6420	0.0286	6356
0.0389	6015	0.0378	6430	0.350	6405

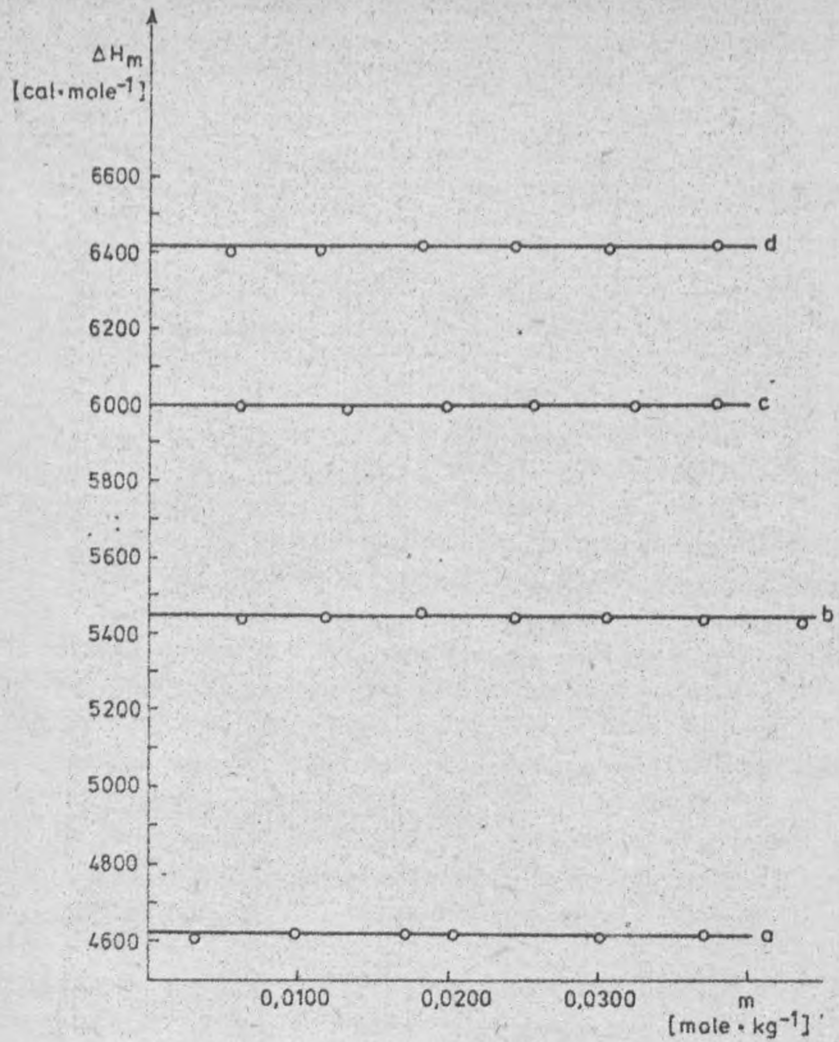

Fig. 1. The relation between the enthalpy of solution of acetophenone in: a - methanol, b - butanol-1, c - 2-methyl-propanol-1, d - butanol-2 and concentration at 286,16 K

Discussion of the results

In the works cited earlier [5-7] the concentration dependence of the enthalpy of solution of the benzoic acid and benzamide in the aliphatic alcohols is linear. In all cases the inclinations of the rectilinear course of the mentioned function are quite remarkable except for the methanol solutions where the straight lines are parallel to the concentration axis. Investigations of the solution enthalpies of the methanol solutions of the benzoic acid, as well as some other data, e. g. vapour pressure and molal volume, indicate that those solutions behave like the thermodynamically ideal ones [9]. In the opinion of the cited authors [5-7]. Both concentration-dependence variations of the benzoic acid and benzamide solution enthalpy and the ΔH_m^o difference in the investigated alcohols are attributable to non-specific interactions.

From the experimental data obtained in this work and presented in Table 1 and Fig. 1 it follows that the lines representing the dependence of the solution enthalpy on acetophenone concentration in all investigated aliphatic alcohols are not only straight but also within the experimental error, parallel to the concentration axis.

The values of the solution enthalpy of acetophenone (ΔH_m) in the investigated alcohols are dependent on the values of:

- enthalpy of acetophenone crystal lattice,
- enthalpy of formation of the mixed acetophenone-alcohol associates A_xAc [A_x represents molecules of the alcohol (A) associated with the acetophenone molecula (Ac) in a mixed associate],
- enthalpy of breaking H-bonds between the alcohol molecules,
- enthalpy of non-specific interactions which constitute the energetically weakest effect.

The process of alcohol associate disintegration and of alcohol-acetophenone associate formation which occurs in the dilute solutions can be represented disgrammatically as follows:

$$n_kA_k + \dots + n_3A_3 + n_2A_2 \rightleftharpoons n_1A_1$$

$$xA_1 + Ac \rightleftharpoons A_xAc$$

where:

A_1 - non-associated alcohol

A_2, A_3, A_k - various types of alcohol associates

Ac - acetophenone

A_xAc - mixed alcohol-acetophenone associate

n_1, n_2, n_3, n_k, x - stechiometric coefficients.

The equilitrium of these two processes is given by the alcohol dissociation constant (K_A) and the alcohol-acetophenone associate formation constant (K_{A_xAc}), respectively

$$K_A = \frac{a_1^{n_1}}{a_2^{n_2} \cdot a_3^{n_3} \dots a_k^{n_k}} \qquad (1)$$

where:

a_2, a_3, a_k - activity of different - type alcohol associates

a_1 - activity of non - associated alcohol

$$K_{A_xAc} = \frac{a_{A_x Ac}}{a_1^x \cdot a_{Ac}} \qquad (2)$$

where:

a_{A_xAc} - activity of the mixed alcohol-acetophenone associate

a_{Ac} - acetophenone activity

The dominating phenomenon in the solution process is the formation of the mixed acetophenone-alcohol associates.

$$K_{A_xAc} = \frac{m_{A_xAc} \cdot f_{A_xAc}}{m_1^x \cdot f_1^x \cdot m_{Ac} \cdot f_{Ac}} \qquad (3)$$

where:

m_{A_xAc}, m_1, m_{Ac} - concentration at equilibrium of the mixed acetophenone-alcohol associate, non-associated alcohol and acetophenone

f_{A_xAc}, f_1, f_{Ac} - activity coefficients of the mixed associate, non-associated alcohol and of acetophenone

$$f_{A_xAc} = \frac{K_{A_x\,Ac}}{K^s_{A_xAc}} \cdot f_1^x \cdot f_{Ac} \qquad (4)$$

where:

$K^s_{A_xAc}$ - concentration constant for the equilibrium of the mixed associate formation process

With sufficiently great excess of the alcohol relative to the solved acetophenone, the values of the activity coefficients for the associated (f_2, f_3, f_k) and non-associated (f_1) alcohol may be assumed to be constant.

The last equation shows that in dilute solutions the activity coefficient of the mixed associate is a linear function of acetophenone activity coefficient

$$K_{A_xAc} = K^s_{A_xAc} \cdot \frac{f_{A_xAc}}{f_1^x \cdot f_{Ac}} \qquad (5)$$

The thermodynamical equilibrium constant $K_{A_x\,Ac}$, for the process of the mixed A_xAc associate formation is a product of the concentration constant for the equilibrium of the mixed associate formation process characterizing the equilibrium of the ideally associated solution and of an expression related to the activity coefficients. This expression represents the deviation of the A_xAc associate formation process equilibrium from the equilibrium of that process in the ideally associated solution. From Eq. 4 it follows that a part of the free enthalpy of solution of acetophenone attributable to the non-specific interaction forces is a linear function of acetophenone solution concentration.

$$a_{A_xAc} = K_{A_xAc} \cdot a_1^x \cdot a_{Ac} \qquad (6)$$

With sufficiently great alcohol excess, the activities of the non-associated alcohol, a_1 and of the alcohol associates (a_2, a_3, a_k) can be assumed to be almost constant (the condition of the system is close to that of the pure solvent).

From relations 4 and 6 it follows that also that portion of the free solution enthalpy which relates to the alcohol H-bond breaking and acetophenone-alcohol associate formation process is linearly dependent on acetophenone concentration. The linear course of the solution enthalpy and of the free solution enthalpy implies linear dependence of the expression $T\Delta S_m$ on acetophenone solution concentration. The expression $T\Delta S_m$ relates to the change of entropy in the solution process.

With infinitely large value of the equilibrium constant (K_{A_xAc}) of the mixed associate formation process and with very small acetophenone concentrations it is possible to assume that the whole quantity of acetophenone forms the mixed associates with the alcohol.

$$Ac + xA_1 \longrightarrow A_xAc$$

This solution behaves like an apparently ideal one. Within the range of very small concentrations the interactions between the molecules in the mixed associate and between the alcohol and the molecules of the mixed associate are not preceptibly changed. Very large alcohol quantity relative to that of acetophenone causes that the non-associated alcohol concentration change (Δm_1) in the process of mixed (A_xAc) associate formation constitutes only a small percentage of its total concentration (m_1). The number of H-bonds broken in the alcohol and the number of H-bonds created in the process of formation of one mole of the mixed associate remains constant and is independent of the concentration. The free enthalpy associated with these processes is constant. Constant within the experimental error values of the acetophenone solution enthalpy and of the free enthalpy imply that the energetic expression $T\Delta S_m$ relating to solution entropy change is also constant. Within the investigated concentration range, the enthalpy of solution of acetophenone is equal to the enthalpy of solution of acetophenone in an anfinitely dilute solution ($\Delta H_m = \Delta H_m^{\infty}$) as can be seen from Fig. 1 and from the experimental data in Table 1.

The molal enthalpy of solution of acetophenone under constant conditions of temperature and pressure may be considered to consist of the following shares:

$$\Delta H_m = \Delta H_m^{\infty} = \Delta H_K + \Delta H_{m(a)} + \Delta H_{m(n)}$$

where:

ΔH_K - enthalpy of the crystal lattice disordering

$\Delta H_{m(a)}$ - enthalpy of formation of one mole of the mixed

$\Delta H_{m(n)}$ - molal enthalpy of the non-specific interactions

If we assume that all investigated aliphatic alcohols form with acetophenone, associates of similar type (A_xAc) and that the effect of the hydrocarbon chain length on H-bond energy is negligible the relative molal enthalpies of the non-specific interactions would then be determined by the differences between the first molal enthalpies of solution of acetophenone in those alcohols.

$$\Delta(\Delta H_m)_w = (\Delta H_m)_1 - (\Delta H_m)_2$$

where:

$\Delta(\Delta H_m)_\omega$ - relative molal enthalpy of the non-specific interactions

1, 2 - indexes relating to the two different alcohols.

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MOLOWA ENTALPIA ROZPUSZCZANIA ACETOFENONU W ALKOHOLACH ALIFATYCZNYCH W TEMPERATURZE 286,16 K

Zmierzono wartości entalpii rozpuszczania acetofenonu w metanolu, n-butanolu, izobutanolu (2-metylo-propanolu-1) i butanolu-2 w przedziale stężeń od ok. 0,003 mol/kg do ok. 0,043 mol//kg w temperaturze 286,16 K. Stwierdzono, że entalpia rozpuszczania acetofenonu w badanych alkoholach nie zależy od stężenia. Określono entalpię rozpuszczania acetofenonu w badanych alkoholach w rozcieńczeniu nieskończenie wielkim.

Ежи Мокжан

ИНТЕГРАЛЬНАЯ ЭНТАЛЬПИЯ РАСТВОРЕНИЯ АЦЕТОФЕНОНА В АЛИФАТИЧЕСКИХ СПИРТАХ ПРИ ТЕМПЕРАТУРЕ 286,16 К

Измерена энтальпия растворения ацетофенона в метаноле, н-бутаноле, изобутаноле, 2-метил-пропаноле-1 и бутаноле-2 в пределах концентрации 0,003 мол/кг до 0,043 мол/кг при темпиературе 286,16 К. Оказалось что энтальпия растворения ацетофенона в исследованных спиртах не зависит от концентрации. Определена энтальпия растворения ацетофенона в исследованных спиртах при бесконечном разбавлении.