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# MOLAL SOLUTION ENTHALPY OF BENZOPHENONE IN ALIPHATIC ALCOHOLS AT 286.16 K AND 298.16 K

The values of the solution enthalpy of benzophenone in methanol, n-butanol, 2-methylpropanol-1 and butanol-2 have been measured within the range from ca. 0.002 mol. $kg^{-1}$ to ca 0.04 mol. $kg^{-1}$ concentration range at 286.16 K and 298.16 K. It has been found that the solution enthalpy of benzophenone in the investigated alcohols in the above concentration range is constant within the experimental error.

The enthalpy and equilibrium constant of benzoic acid association in the non-polar solvents were investigated by many authors [1, 2, 3]. The work performed in our laboratory related to investigating the properties of benzoic acid solutions in the polar and non-polar solvents [4, 5, 6, 7, 8]. The results of the investigations indicate that, in the aliphatic alcohols, benzoic acid forms type $AB_2$ mixed associates (A - benzoic acid, B - alcohol) [6]. The course of the dependence the solution enthalpy of the benzoic acid and benzamide vs. concentration $\Delta H_m = f(m)$, in the aliphatic alcohols is linear. The inclination of the lines to the concentration axis is remarkably greater for benzoic acid than for benzamide [5, 7, 8]. Recent measurements of the solution enthalpy of acetophenone in the aliphatic alcohols at 286.16 K have shown that, within the experimental error, the solution enthalpy of acetophenone in the concentration range below 0.04 mol. $kg^{-1}$ is independent of temperature [9].

## EXPERIMENTAL

Benzophenone (Krakówskie Zakłady Farmaceutyczne "Polfa") was distilled under 10 mm Hg vaccum. The fraction boiling at 437.66 K to 438.16 K was collected. The melting point of the benzophenone was 321.16 K.

Methanol, analytical grade, was dried by the Lund-Bjerrum method [10], n-butanol, 2-methylpropanol-2 and butanol-2 were dried using calcium oxide and then distilled in a distillation column.

A non-isothermal non-adiabatic calorimeter was used for heat measurements. A glass calorimeter had been provided with type N. T. C. high-resistance thermistors. Wheatston bridg unbalance voltage variations were recorded by means of a Meratronik V534 digital voltmeter. Under the conditions of the measurement, the bridge unbalance voltage variations were a linear function of the calorimeter temperature variations. The precision of the calorimetric measurements was $\pm 20$ cal. mol.$^{-1}$ (1 cal. = 4.184 J).

## EXPERIMENTAL RESULTS

The values of the solution enthalpy of benzophenone in the investigated alcohols at 286.16 K and 298.16 K are presented in tab. 1, 2, fig. 1, 2 represent the course of the dependence of benzophenone solution enthalpy in the aliphatic alcohols.

Table 1

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

| Methanol | | n-buthanol | |
|---|---|---|---|
| m $mol. kg^{-1}$ | $\Delta H_m$ $J. mol^{-1}$ | m $mol. kg^{-1}$ | $\Delta H_m$ $J. mol^{-1}$ |
| 0.0000 | 21606 | 0.0000 | 24058 |
| 0.0043 | 21635 | 0.0040 | 24008 |
| 0.0085 | 21615 | 0.0078 | 24016 |
| 0.0124 | 21569 | 0.0117 | 24129 |
| 0.0167 | 21564 | 0.0151 | 24108 |
| 0.0243 | 21569 | 0.0190 | 24045 |
| 0.0292 | 21573 | | |
| 0.0332 | 21570 | | |
| **2-methylopropanol-1** | | **buthanol-2** | |
| 0.0000 | 25690 | 0.0000 | 28305 |
| 0.0040 | 25665 | 0.0041 | 28317 |
| 0.0081 | 25627 | 0.0082 | 28326 |
| 0.0123 | 25669 | 0.0121 | 28330 |
| 0.0166 | 25694 | 0.0162 | 28330 |
| 0.0209 | 25706 | 0.0204 | 28284 |
| 0.0249 | 25723 | 0.0245 | 28294 |
| 0.0291 | 25698 | 0.0287 | 28301 |
| 0.0331 | 25702 | | |

Table 2

The values of the molal solution enthalpy of benzophenone in the aliphatic alcohols at 298.16 K

| Methanol | | b-buthanol | |
|---|---|---|---|
| m mol. kg$^{-1}$ | $\Delta H_m$ J. mol.$^{-1}$ | m mol. kg$^{-1}$ | $\Delta H_m$ J. mol.$^{-1}$ |
| 0.0000 | 23535 | 0.0000 | 26568 |
| 0.0025 | 23581 | 0.0024 | 26535 |
| 0.0049 | 23573 | 0.0049 | 26568 |
| 0.0074 | 23518 | 0.0073 | 26522 |
| 0.0098 | 23518 | 0.0096 | 26531 |
| 0.0124 | 23514 | 0.0119 | 26518 |
| 0.0149 | 23527 | 0.0143 | 26493 |
| 2-methylopropanol-1 | | buthanol-2 | |
| 0.0000 | 28535 | 0.0000 | 30731 |
| 0.0024 | 28585 | 0.0024 | 30832 |
| 0.0048 | 28539 | 0.0049 | 30669 |
| 0.0071 | 28539 | 0.0075 | 30690 |
| 0.0095 | 28602 | 0.0098 | 30719 |
| 0.0120 | 28581 | 0.0121 | 30673 |
| 0.0143 | 28568 | 0.0145 | 30694 |

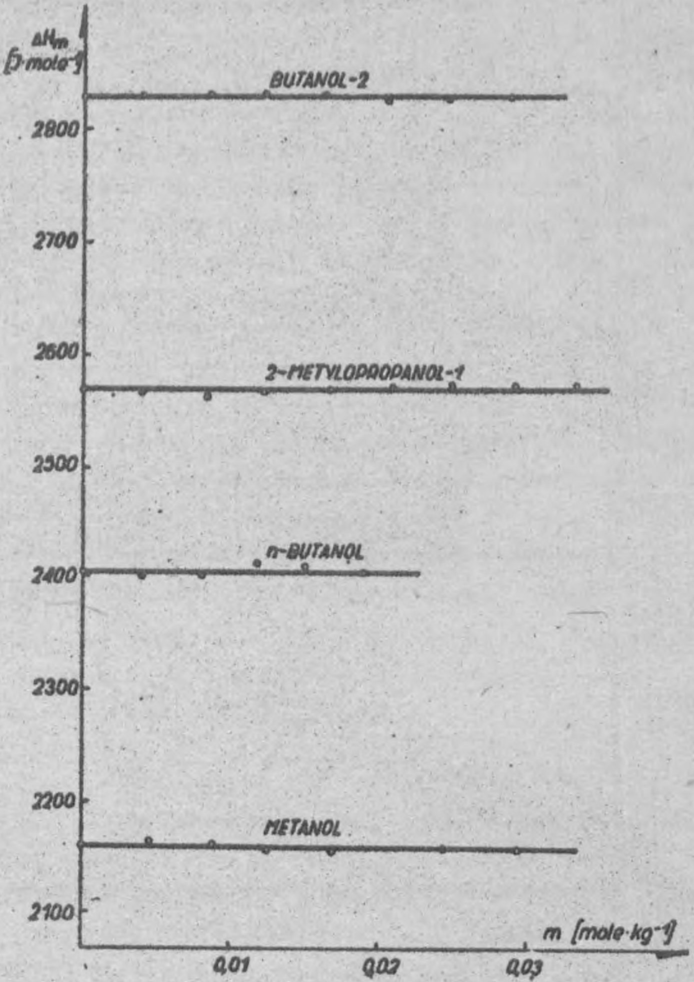

Fig. 1. The concentration-dependence of the solution enthalpy of benzophenone in the investigated aliphatic alcohols at 286.16 K

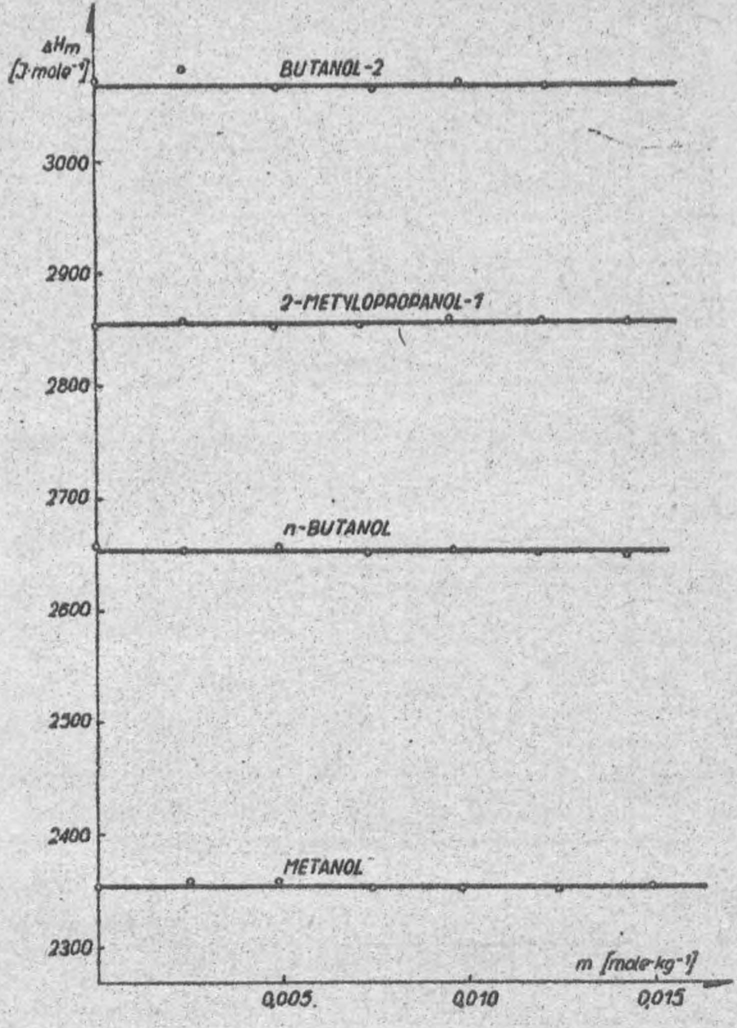

Fig. 2. The concentration-dependence of the solution enthalpy of benzophenone in the investigated aliphatic alcohols at 298.16 K

## DISCUSSION OF THE RESULTS

According to the authors of the papers mentioned above [5, 6, 7] the linear dependence of benzoic acid and benzamide solution enthalpy on the concentration as well as the differences between the standard solution enthalpies $\Delta H_m$ in the investigated aliphatic alcohols are associated with non-specific interaction forces.

The values of benzophenone solution enthalpies presented in tab. 1, 2 and in fig. 1, 2 are independent on the concentration in all investigated aliphatic alcohols. The same linear and within the experimental error, parallel course of the solution enthalpy vs. concentration function $\Delta H_m = f(m)$, has been observed in the investigated aliphatic alcohols also for acetophenone solution enthalpy [9].

The process of solving benzophenone in alcohols is very complex. The solution process is affected primarily by formation of the mixed $A_xB$ alcohol-benzophenone associates ($A_x$ denotes x molecules of alcohol A associated with benzophenone molecule B in the mixed associate), as well as by the accompanying phenomenon of alcohol associate disintegration.

For large values of the equilibrium constant $K_{A_xB}$ of the mixedassociate formation process and small benzophenone to alcohol ratios all of the benzophenone may be assumed to form the mixed associate with alcohol.

$$B + xA \longrightarrow A_xB$$

Within the investigated benzophenone concentration range, the magnitudes of the non-specific interaction forces between the mixed associate molecules themselves and between the alcohol on one hand and the mixed associate molecules on the other do not undergo any evident changes. The very large quantity of alcohol in relation to benzophenone causes that the change of unassociated alcohol concentration ($\Delta m_A$) in the process of mixed-associate formation constitutes only a small fraction of its total concentration ($m_A$). In the process of formation of a mole of the mixed associate, the number of the new-formed H-bonds and the number of the alcohol H-bonds which become disintegrated is constant within the investigated concentration range. The free molal enthalpy associated with these processes is constant. From the measurements performed it follows that the values of benzophenone solution enthalpy are, within the investigated concentration range, equal to the solution enthalpy in an infinitely diluted solution, $\Delta H_m = \Delta H_m^{\infty}$. The constancy of the enthalpy and of the free enthalpy [9] results in the constancy of the expression $T\Delta S$ connected with the change of entropy in the process of solution. The molal solution enthalpy of benzophenone under constant pressure can be interpreted as a sum of the following contributions:

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

where:

$\Delta H_K$ - enthalpy of destruction of the crystal lattice of one mole of benzophenone;

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

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

If we assume, like for acetophenone [9], that all investigated aliphatic alcohols form with benzophenone mixed associates of the same type $(A_xB)$, and that the effect of the hydrocarbon chains on the H-bond energy is negligible, the differences between the standard molal solution enthalpies of benzophenone in those alcohols should determine the relative molal enthalpies of the non-specific interactions:

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

where:

$\Delta(\Delta H_m)$ - relative molal enthalpy of non-specific interactions;

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

The investigations [5, 6, 7] relating to benzoic acid and benzamide, and the performed measurements of acetophenone solution enthalpy favour the opinion that the differences of the first heats of solution in the investigated alcohols determine the non-specific interaction enthalpies.

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## MOLOWA ENTALPIA ROZPUSZCZANIA BENZOFENONU W ALKOHOLACH ALIFATYCZNYCH W TEMPERATURACH 286,16 K i 298,16 K

Zmierzono wartości entalpii rozpuszczania benzofenonu w metanolu, n-butanolu, izo-butanolu (2-metylopropanolu-1) i butanolu-2 w zakresie stężeń od około 0,002 mol. $kg^{-1}$ do około 0,04 mol. $kg^{-1}$ w temperaturze 286,16 K i 298,16 K. Ustalono, że entalpia rozpuszczania benzofenonu w badanych alkoholach w wymienionym przedziale stężeń w granicach błędu eksperymentalnego jest stała.

Ежи Мокжан

## ИНТЕГРАЛЬНАЯ ЭНТАЛЬПИЯ РАСТВОРЕНИЯ БЕНЗОФЕНОНА В АЛИФАТИЧЕСКИХ СПИРТАХ ПРИ ТЕМПЕРАТУРЕ 286,16 и 298,16 К

Измерена энтальпия растворения бензофенона в метаноле, н-бутаноле, 2-метил-пропаноле-I и бутаноле-2 в пределах концентрации 0,002 мол(кг до 0,04 мол)кг при температуре 286,16 и 298,16 К. Оказалось что энтальпия растворения бензофенона в исследованных спиртах не зависит от концентрации. Спределена энтальпия растворения бензофенона в исследованных спиртах при бесконечном разбавлении.