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RELATIONSHIP BEETWEN THE ENTHALPY OF TRANSFER OF A SOLUTE AND THE THERMODYNAMIC MIXING FUNCTIONS OF MIXED SOLVENT COMPONENTS

On the basis of date on the enthalpy of solutions, ΔH_s^o, of $CaCl_2$ and NaI in aqueous mixtures of methanol, ethanol and propan-1-ol and of NaCl and KCl in water + tetrahydrofuran mixtures - the enthalpy of transfer, ΔH_t^o, of the solutes from water to mixtures has been calculated. The dependence of ΔH_t^o on the solvent composition has been compared with the analoqous relationship for the enthalpy of mixing, ΔH^E, of the two solvent components. The correlation suggested by Feakins between: $\Delta H_t^o/x_2 = F(\Delta H^E/x_2)$ has not been found linear in the whole rich region.

DISCUSSION

The appearence of extremal values of some thermodynamic functions (and also of several physicochemical properties) is characteristic for solutions of salts in water-alcohol solvents as well as for solvents themselves.

For example: investigations performed earlier [1, 2] proved that the enthalpies of transfer, ΔH_t^0, of alcali-metal halides from water to water-methanol mixtures pass trough pronauced maxima in the water rich region ($0.1 < x_2 < 0.2$). The enthalpy of mixing, ΔH^E, of the two solvent components [3, 4] exhibits minimum corresponding to x_2 ca. 0.3 of methanol (Fig. 1).

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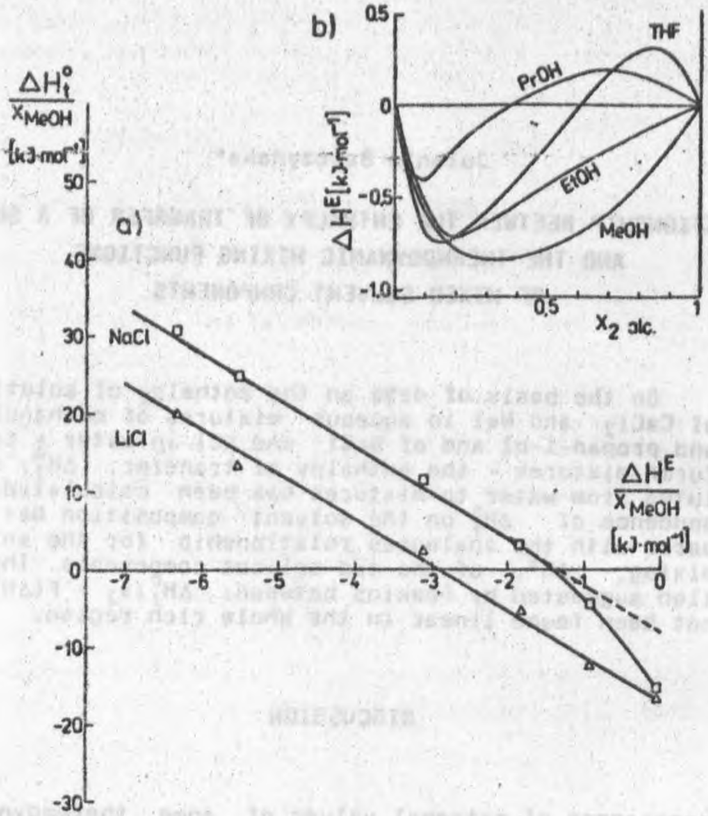

Fig. 1. a) Plots of $\Delta H_t^0/x_{MeOH}$ against $\Delta H^E/x_{MeOH}$ for Δ LiCl and □ NaCl in methanol-water solvent systems from ref. [5] and b) enthalpies of mixing ΔH^E ploted against the mol fraction of alcohols in methanol-water; ethanol-water; propan-1-ol + water and tetrahydrofuran-water systems [12]

Feakins and co-workers [5] made an effort to correlate both thermodynamic functions for the methanol-water-alcali metal halides systems. By means of theoretical considerations the autors predicted the linear correlation of the standard transfer enthalpy of electrolytes from water to the mixed solvent, ΔH_t^0, and the enthalpy of mixing of water with alcohol, ΔH^E, according to equation:

$$\Delta H_t^o = -a\Delta H^E + x_B b$$

or

$$\frac{\Delta H_t^o}{x_B} = -a\frac{\Delta H^E}{x_B} + b \tag{1}$$

where:

a, b - parameters of the straight line,

x_B - mol fraction of alcohol.

It turned out that in water-methanol solutions of alkali metal chlorides expression (1) is fulfilled over the whole range of the binary solvent compositions only for LiCl-water-methanol system (Fig. 1). In the case of other chlorides good linearity is shown

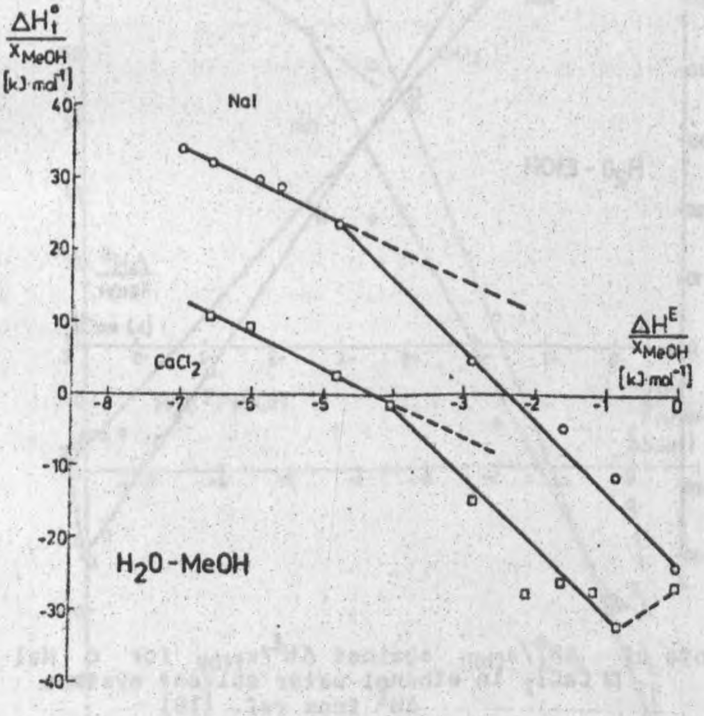

Fig. 2. Plots of $\Delta H_t^o/x_{MeOH}$ against $\Delta H^E/x_{MeOH}$ for o NaI and □ $CaCl_2$ in methanol-water solvent systems ΔH^E from ref. [10]

for $0 < x_2 < 0.7$ in NaCl solutions and for $0 < x_2 < 0.45$ in KCl solutions [5]. According to the authors [5] the maxima observed in ΔH_t^0 curves seem to be only a consequence of the appearance of minima of the enthalpy of mixing vs. alcohol content corresponding to the stabilization of water structure. Therefore, maxima of ΔH_t^0 do not prove the change of structure resulting from the effect of electrolyte solvation on the solvent structure.

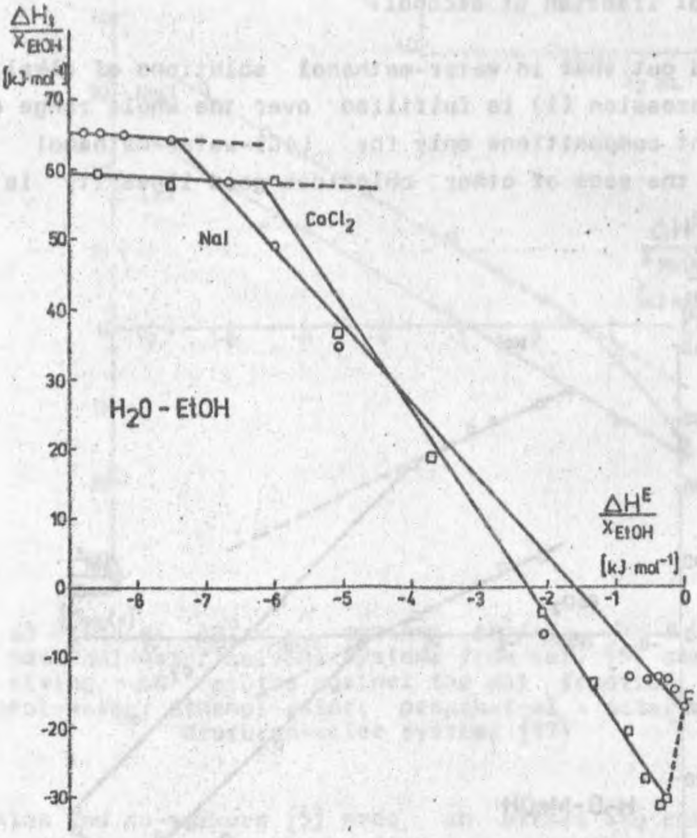

Fig. 3. Plots of $\Delta H_t^0/x_{EtOH}$ against $\Delta H^E/x_{ETOH}$ for ○ NaI and □ $CaCl_2$ in ethanol-water solvent systems ΔH^E from ref. [10]

In this work we tried to apply the proposed correlation in water-alcohol mixtures for electrolytes 1 : 1 type i.e NaI [6] and 2 : 1 type i.e. $CaCl_2$ [7] and in water-THF mixtures for NaCl and KCl [8, 9]. The results of using eqn. 1 for water-methanol solutions of NaI and $CaCl_2$ are presented in Fig. 2. According to the suggestion of the autors [5] Fig. 2 shows the plots of $\Delta H_t^o/x_{CH_3OH}$ against $\Delta H^E/x_{CH_3OH}$; ΔH^E from ref. [10].

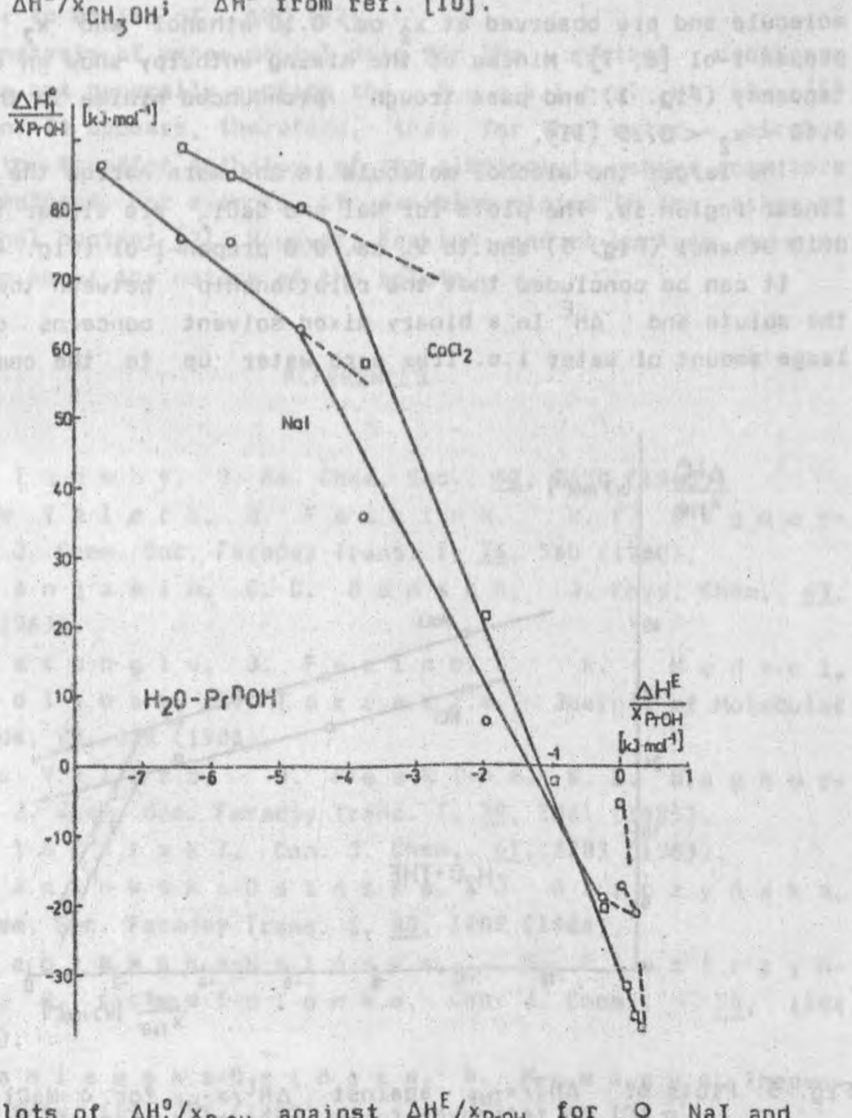

Fig. 4. Plots of $\Delta H_t^o/x_{PrOH}$ against $\Delta H^E/x_{PrOH}$ for ○ NaI and □ $CaCl_2$ in propan-1-ol + water solvent systems ΔH^E from ref. [13]

As it is seen for NaI and $CaCl_2$ solutions the linear correlation between two thermodynamic functions is observed only within the range $0 < x_2 < 0.2$ methanol i.e. to such concentration of methanol in water which corresponds to the maxima of the ΔH_t^o [6, 7].

Maxima of the transfer enthalpy shift towards the smaller alcohol content together with the increase of the size of alcohol molecule and are observed at x_2 ca. 0.10 ethanol and x_2 ca. 0.8 propan-1-ol [6, 7]. Minima of the mixing enthalpy show an analoqous tendency (Fig. 1) and pass trough pronounced minima in the region $0.10 < x_2 < 0.15$ [11].

The larger the alcohol molecule is the more narrow the straight linear region is. The plots for NaI and $CaCl_2$ are linear to x_2 ca. 0.10 ethanol (Fig. 3) and to x_2 ca. 0.8 propan-1-ol (Fig. 4).

It can be concluded that the relationship between the ΔH_t^o of the solute and ΔH^E in a binary mixed solvent concerns only the large amount of water i.e. from pure water up to the composition

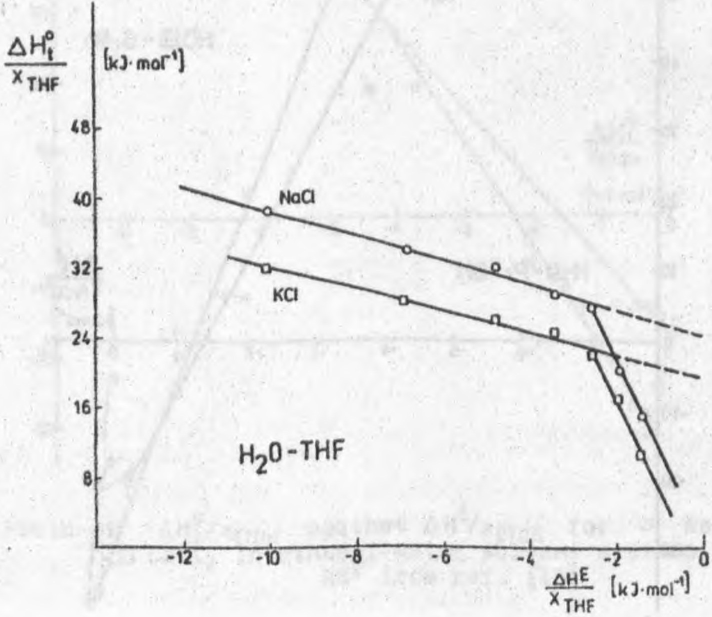

Fig. 5. Plots of $\Delta H_t^o/x_{THF}$ against $\Delta H^E/x_{THF}$ for ○ NaCl and □ KCl in tetrahydrofuran-water solvent systems ΔH^E from ref [12]

corresponding to maximum of ΔH_t^o. It seem that the correlation proposed by Feakins et al. depends distinclly on extrema of curves $\Delta H_t^o = f(x_2)$.

This conclusion is supported by investigations of NaCl and KCl solutions in tetrahydrofuran-water mixtures. The linear plot does not exceed the composition range $0 < x_2 < 0.25$ of THF (Fig. 5) i.e. from water to maxima of ΔH_t^o [12].

The analysis of experimental data for the systems mentioned above does not generally confirm the Feakins' et al. [5] suggestion. It appears, therefore, that for the water - alcohol systems, the transfer enthalpy of the electrolyte shows some more complex features. For example, it exhibits minima in the range of high alcohol content [7]. However, Feakins and co-workers make no assumption about the nature of the solute.

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ZALEŻNOŚĆ MIĘDZY ENTALPIĄ PRZENIESIENIA SUBSTANCJI ROZPUSZCZONEJ A TERMODYNAMICZNYMI FUNKCJAMI MIESZANIA ROZPUSZCZALNIKÓW

Na podstawie danych entalpii rozpuszczania, ΔH_s^o, elektrolitów: $CaCl_2$ oraz NaI w mieszaninach wody z metanolem, etanolem i n-propanolem (propan-1-ol), a także NaCl i KCl w mieszaninach wody z tetrahydrofuranem obliczono entalpie przeniesienia, ΔH_t^o, wymienionych elektrolitów z wody do mieszanych rozpuszczalników. Porównano przebieg zależności ΔH_t^o i ΔH^E w funkcji składu badanych mieszanin. Sprawdzając koncepcję Feakinsa podjęto próbę korelacji: $\Delta H_t^o / x_2 = f(\Delta H^E / x_2)$ we wszystkich analizowanych układach i stwierdzono, że liniowa zależność między funkcjami termodynamicznymi nie obejmuje całego zakresu składów badanych mieszanin.