ACTA UNIVERSITATIS LODZIENSIS
FOLIA CHIMICA 10, 1993

Bożenna Nowicka*, Henryk Piekarski*

# MEDIUM EFFECTS ON TRANSFER ENTHALPIES OF ELECTROLYTES FROM WATER TO ORGANIC SOLVENTS AND TO WATER-ORGANIC MIXTURES

Enthalpies of transfer, $\Delta_{tr}H^{\infty}$ of electrolytes from water to several organic solvents were correlated with parameters describing some properties of the solvents. The influence of both cation and anion kind and size on the relative contributions of the solvent properties to the observed variation of the $\Delta_{tr}H^{\infty}$ of the salts was analysed. The similar correlations of transfer enthalpies of salts from water to water-organic mixtures with a composition corresponding to observed $\Delta_{tr}H^{\infty}$ maximum were examined.

## INTRODUCTION

Thermochemical properties of electrolyte solutions in non-aqueous and mixed water-organic solvents depend, to large extent on physico-chemical properties of the organic component. In the former case, the differences in dissolution, or better in solvation enthalpies of the solute reflect variation of the organic solvent properties. In the latter case, the dissolution enthalpies $\Delta_{sol}H^{\infty}$ as a function of the mixed solvent composition often exhibit a complex shape with characteristic maxima within the water-rich region. The appearance of these maxima in some water-organic mixtures is generally attributed to the change of the mixed solvent structure or to the hydrophobic hydration and

---

* Department of Physical Chemistry, University of Łódź, Pomorska 18, 91-416 Łódź, Poland.

overlaping of the hydrophobic cospheres. Therefore, the mixed solvent with a composition corresponding to the $\Delta_{sol}H^{\infty}$ maximum has some special features. The height of the maximum on the $\Delta_{sol}H^{\infty}$ = f (mixed solvent composition) curve in a given mixture depends on the kind of dissolved salt. On the other hand, for the same electrolyte dissolved in different mixed solvents the heights of the mentioned $\Delta_{sol}H^{\infty}$ maxima also differ significantly from each other. As an illustration of this behavior the enthalpies of transfer, of $NaBPh_4$ from water to several water-organic mixtures, $\Delta_{tr}H^{\infty}$ defined as:

$$\Delta_{tr}H^{\infty} = \Delta_{sol}H^{\infty}(\mathrm{Mixt}) - \Delta_{sol}H^{\infty}(\mathrm{Water}) \qquad (1)$$

are presented in Fig. 1 as a function of the mixed solvent composition.

In order to obtain some informations about the factors that influence the observed properties of the system, the so-called multiple linear regression analysis (MLRA) can be applied. In this approach, the analysed function (for instance the enthalpy of transfer) is correlated with the parameters describing selected properties of the system components. Having at our disposal a number of data on the dissolution enthalpies of electrolytes in different organic and mixed water-organic solvents[1] we decided to check whether the use of the mentioned MLRA method enables finding which of the solvent properties and to what extent influence the observed thermochemical behavior of the solutions. Moreover, from obtained correlation equations referring to different electrolytes we expected to conclude about the influence of the kind of ion on the relative contribution of the solvent properties to the total variation of the $\Delta_{tr}H^{\infty}$ values within the examined set of solvents.

Numerous multiparametric correlation equations are described in the literature. The Koppel-Palm [2], Krygowski-Fawcett [3, 4] and Abraham-Kamlet-Taft [5-7] ones belong to the best known. All the mentioned equations

---

[1] The appropriate data were taken from ref. [1] unless stated otherwise.

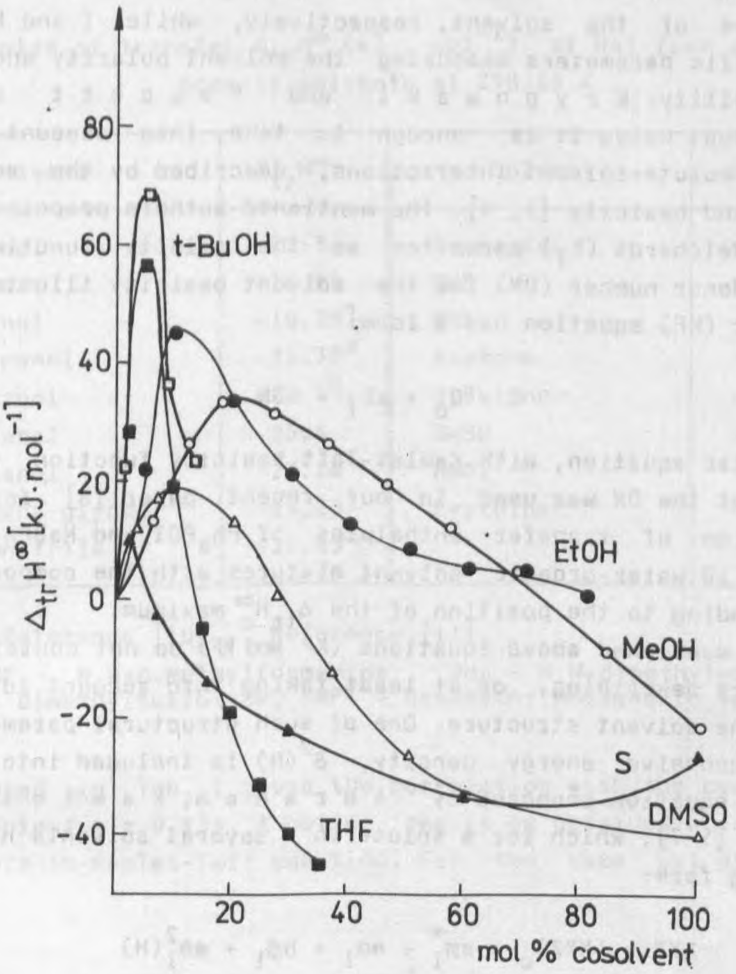

Fig. 1. Enthalpies of transfer, $\Delta_{tr}H^{\infty}$ of NaBPh$_4$ from water to water-organic solvent mixtures. MeOH - methanol, EtOH - ethanol, t-BuOH - tert-butanol, THF - tetrahydrofuran, DMSO-dimethylsulfoxide, S-sulfolane

are a linear combination of selected parameters describing some properties of the system components, but they contain different number and different kind of the parameters. The Koppel-Palm [2] equation has a form:

$$Q = Q_o + \alpha A + \beta B + \eta Y + \pi P \qquad (2)$$

where A and B are parameters measuring the acceptor and donator properties of the solvent, respectively, while Y and P are non-specific parameters measuring the solvent polarity and its polarizability. Krygowski and Fawcett showed that in most cases it is enough to take into account only specific solute-solvent interactions, described by the solvent acidity and basicity [3, 4]. The mentioned authors proposed the Dimroth-Reichardt ($E_T$) parameter as the acidity function and Gutmann donor number (DN) for the solvent basicity illustration and their (KF) equation has a form:

$$Q = Q_o + aE_T + bDN \tag{3}$$

The similar equation, with Kamlet-Taft basicity function ($\beta_{KT}$) instead of the DN was used in our recent paper [8] for the correlation of transfer enthalpies of $Ph_4PCl$ and $NaBPh_4$ from water to 10 water-organic solvent mixtures with the composition corresponding to the position of the $\Delta_{tr}H^\infty$ maximum.

Both mentioned above equations (KP and KF) do not contain any parameters describing, or at least taking into account to some extent the solvent structure. One of such structural parameters, namely cohesive energy density, $\delta^2(H)$ is included into correlation equation proposed by Abraham, Kamlet and Taft [5-7], which for a solute in several solvents has the following form:

$$XYZ = (XYZ)_o + s\pi_1^* + a\alpha_1 + b\beta_1 + m\delta_1^2(H) \tag{4}$$

where $\pi_1^*$ is a parameter designating the solvent dipolarity/polarizability, $\alpha_1$ and $\beta_1$ denote acidity and basicity parameter of the solvent and $\delta_1^2(H)$ is its cohesive energy density.

## RESULTS

### a. Enthalpies of transfer of NaI from water to pure organic solvents.

The application of the Koppel-Palm equation for transfer enthalpies, $\Delta_{tr}H^\infty$ of NaI from water to 17 organic solvents

Table 1

Enthalpies of transfer $\Delta_{tr}H^{\infty}$ ($kJ \cdot mol^{-1}$) of NaI from water to organic solvents at 298.15 K

| Solvent | $\Delta_{tr}H^{\infty}$ | Solvent | $\Delta_{tr}H^{\infty}$ |
|---|---|---|---|
| Methanol | -22.3 | Formamide | -23.48 |
| Ethanol | -16.95 | DMF | -47.53 |
| Propanol | -18.79[a] | DMA | -44.18 |
| 2-Propanol | -21.39[a] | Acetone | -35.93 |
| n-Butanol | -21.7[b] | 2-Butanon | -33.5 |
| i-Butanol | -25.6 | DMSO | -40.63 |
| 2-Butanol | -26.14 | HMPT | -58.63 |
| Ethylene glycol | -24.23 | Pyridine | -43.0 |
| Acetonitrile | -21.63 | | |

[a] Reference [10]. [b] Reference [11].

DMF - N,N-dimethylformamide, DMA - N,N-dimethylacetamide, DMSO - dimethylsulfoxide, HMPT - hexamethylphosphoric triamide.

presented in Tab. 1 gives the correlation with the correlation coefficient r = 0.936. A better result is obtained when we use the Abraham-Kamlet-Taft equation. For the same set of data we have:

$$\Delta_{tr}H^{\infty} = -(43.1 \pm 8.1)\pi_1^* + (8.8 \pm 6.0)\alpha_1 - (21.5 \pm 5.6)\beta_1 + (0.08 \pm 0.03)\delta_1^2(H) \qquad (5)$$

with r = 0.966, disp. = 3.91.

As it is known the $\alpha$ scale of acidity describes the ability of a molecule to donate a proton in a solute-to-solvent hydrogen bond [5-7]. For the ionic solutions the application of $\alpha$ scale can be doubtful. Therefore we have replaced this parameter in the AKT equation by $E_T$—Dimroth-Reichardt acidity function. This replacement practically does not influence the accuracy of the fit. The obtained equation that correlates best with the $\Delta_{tr}H^{\infty}$ NaI values has following form:

$$\Delta_{tr}H^{\infty} = -(56.6 \pm 4.4)\pi_1^* + (0.21 \pm 0.14)E_T -$$
$$- (21.2 \pm 5.1)\beta_1 + (0.10 \pm 0.02)\delta_1^2(H) \qquad (6)$$

with r = 0.967, disp. = 3.88.

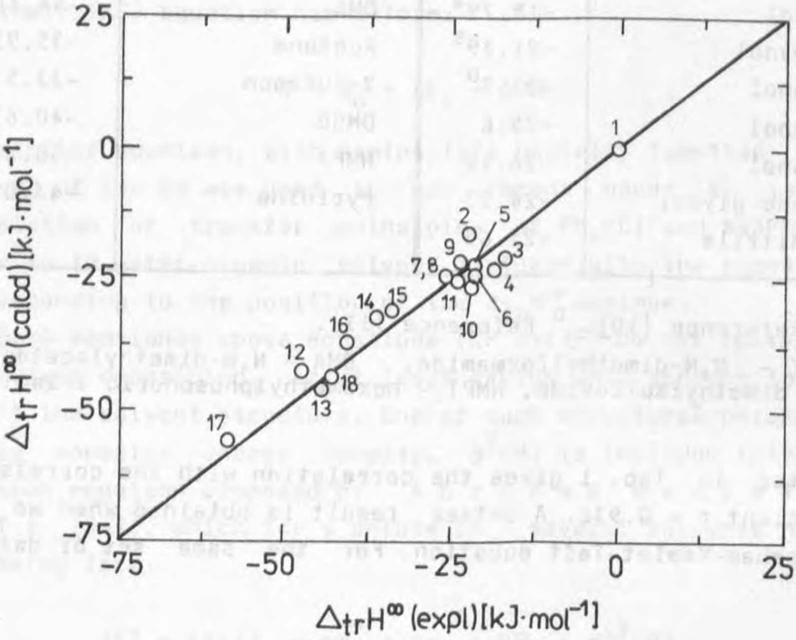

Fig 2. Comparison of the NaI transfer enthalpies from water to organic solvents determined experimentally and calculated from eq. 5

1 - water; 2 - methanol; 3 - ethanol; 4 - propanol; 5 - 2-propanol; 6 - butanol; 7 - i-butanol; 8 - 2-butanol; 9 - ethylene glycol; 10 - acetonitrile; 11 - formamide; 12 - N,N-dimethylformamide; 13 - N,N-dimethylacetamide; 14 - acetone; 15 - 2-butanon; 16 - dimethylsulfoxide; 17 - hexamethylphosphoric triamide; 18 - pyridine

A comparison of the NaI transfer enthalpies determined experimentally with those calculated from the above equation is given in Fig. 2. The numerical values of the parameters characterising the analysed solvents were taken from ref. [9].

**b. Enthalpies of transfer of other electrolytes from water to pure organic solvents.**

In order to compare the influence of the cation and/or the anion change on the presented correlation we performed the analogous calculations for the transfer enthalpies of other salts having the same cation or the anion. The transfer enthalpies are known only for limited number of different solvents. Therefore, we have correlated the enthalpies of transfer, $\Delta_{tr}H^{\infty}$ for the salts: NaI, $NaBPh_4$, $NaClO_4$, KI, $Ph_4AsI$ from water to the same set of organic solvents, namely: methanol, ethanol, n-propanol, acetonitrile, acetone, N,N-dimethylformamide, N,N-dimethylacetamide, dimethylsulfoxide and hexamethylphosphoric triamide, using the equation:

$$\Delta_{tr}H^{\infty} = (\Delta_{tr}H^{\infty})_o + s\pi_1^* + aE_T + b\beta_1 + m\delta_1^2(H) \qquad (7)$$

The obtained values of the coefficients: s, a, b, m and the correlation coefficients, r for each of the salts are presented in Tab. 2. In the same table we collected the relative contributions of the solvent properties, illustrated by $\pi_1^*$, $E_T$, $\beta_1$, and $\delta_1^2(H)$ to the analysed variation of $\Delta_{tr}H^{\infty}$. The two sets of the s, a, b and m values for NaI solutions given in eq. 6 and in Tab. 2 differ each other. This is so since they relate to two different groups of solvents.

**c. Enthalpies of transfer of electrolytes from water to water-organic solvent mixtures.**

As was mentioned earlier we intended to analyse the effect of the organic cosolvent properties on the height of $\Delta_{sol}H^{\infty}$ maxima of electrolytes, characteristic for many aqueous binary mixtures. Therefore, by the use of the MLRA method we correlated the transfer enthalpies of $NaBPh_4$, $Ph_4PCl$ and $Bu_4NBr$ from water to the water-organic cosolvent mixtures, composition of corresponding to the $\Delta_{sol}H^{\infty}$ (or $\Delta_{tr}H^{\infty}$) maximum with the parameters describing the cosolvent features. The same analysis was performed also for NaI solutions in the mixed solvents. The $\Delta_{sol}H^{\infty}$ function for NaI has no maximum in the mixtures of water with acetone, sulfolane and acetonitrile. Therefore, the enthalpies of transfer of this salt from water to the mentioned

Table 2

Coefficients of the equation 5 correlating the enthalpies of transfer of electrolytes from water to organic solvents and percentage contributions of selected properties of solvents to variation of $\Delta_{tr}H^{\infty}$

| Coefficients of eq. 5 | NaI | $NaClO_4$ | $NaBPh_4$ |
|---|---|---|---|
| s | -56.3±8.9 | -73.6±13.3 | -74.7±16.0 |
| a | -0.2±0.2 | (+0.07±0.3) | +0.5±0.4 |
| b | -21.3±9.9 | -15.1±13.4 | -29.7±17.9 |
| m | +0.10±0.03 | +0.15±0.04 | +0.10±0.05 |
| r | 0.967 | 0.969 | 0.938 |
| disp. | 5.35 | 7.04 | 9.97 |
| $\%\pi^*$ | 33 | 32 | 32 |
| $\%E_T$ | 4 | (1) | 8 |
| $\%\beta$ | 17 | 10 | 17 |
| $\%\delta^2(H)$ | 39 | 51 | 30 |
| $n^a$ | 10 | 10 | 10 |

| Coefficients of eq. 5 | KI | $Ph_4AsI$ | $Bu_4NBr$ |
|---|---|---|---|
| s | -68.4±7.0 | -49.3±7.3 | +8.3±5.6 |
| a | - | +0.36±0.16 | +0.75±0.17 |
| b | -5.9±5.3 | (-3.1±7.3) | - |
| m | +0.13±0.01 | +0.06±0.02 | -0.10±0.02 |
| r | 0.975 | 0.957 | 0.948 |
| disp. | 4.42 | 4.20 | 3.53 |
| $\%\pi^*$ | 38 | 42 | 8 |
| $\%E_T$ | - | 10 | 25 |
| $\%\beta$ | 4 | (3) | - |
| $\%\delta^2(H)$ | 53 | 36 | 65 |
| $n^a$ | 10 | 10 | 9 |

[a] Water and 8 or 9 organic solvents as mentioned in the paper.

Table 3

Coefficients of the equation 5 correlating the enthalpies of transfer of electrolytes from water to water-organic mixtures with the composition corresponding to the $\Delta_{tr}H^{\infty}$ maxima of organic salts and percentage contributions of selected properties of solvents to variation of $\Delta_{tr}H^{\infty}$

| Coefficients of eq. 5 | NaI | $Ph_4PCl$ | $NaBPh_4$ | $Bu_4NBr$ |
|---|---|---|---|---|
| $(\Delta_{tr}H^{\infty})_o$ | (-5.2±6.8) | 34.4±10.6 | 108.8±24.3 | (-42.2±48.1) |
| s | -11.4±3.2 | -40.1±5.0 | -50.5±11.5 | 10.6±13.5 |
| a | (-0.10±0.14) | (0.13±0.22) | -1.9±0.5 | 1.4±1.0 |
| b | 10.4±2.2 | 20.2±3.5 | 57.6±8.0 | 34.7±9.6 |
| m | 0.02±0.01 | (-0.01±0.02) | 0.10±0.04 | -0.12±0.06 |
| r | 0.965 | 0.992 | 0.985 | 0.972 |
| disp. | 1.43 | 2.22 | 5.11 | 5.02 |
| n | 11[a] | 11[a] | 11[a] | 9[b] |
| $\%\pi^*$ | 27 | 53 | 20 | (6) |
| $\%E_T$ | (8) | (6) | 25 | 24 |
| $\%\beta$ | 33 | 35 | 30 | 22 |
| $\%\delta^2(H)$ | 25 | (5) | 23 | 43 |

n - number of solvents.

[a] Water and mixtures of water with: methanol, ethanol, n-propanol, isopropanol, tert-butanol, acetone, tetrahydrofuran, hexamethylophosphoric triamide, sulfolane, acetonitrile.

[b] Water and mixtures of water with: ethanol, tert-butanol, acetone, sulfolane, acetonitrile, dimethylsulfoxide, N,N-dimethylformamide, N,N-dimethylacetamide.

The values given in parentheses are statistically unsignificant.

mixtures with the composition corresponding to the $\Delta_{tr}H^{\infty}$ maxima of organic salts were used for this analysis (water-acetone: 10 mol%, water-sulfolane: 2 mol% and water-acetonitrile: 6 mol% of the organic cosolvent). Similarly as for the electrolyte solutions in pure organic solvents, the modified AKT equation (eq. 7) was applied here. Since the organic component of the mixed solvent within the high water content can be assumed as one of the solutes (an electrolyte is the other one), the values of the $\pi_1^*$, $E_T$, $\beta_1$, and $\delta_1^2(H)$ parameters were taken the same as for pure organic compounds. The obtained values of s, a, b and m coefficients, the regression coefficient, r and the relative contributions of the solvent properties to the examined variation of $\Delta_{tr}H^{\infty}$ are presented in Tab. 3.

## CONCLUSIONS

It is possible to correlate the transfer enthalpies of electrolytes from water to different organic solvents with the parameters characterising these solvents. Also the enthalpies of transfer of salts from water to the water-organic mixtures, composition of corresponding to the $\Delta_{tr}H^{\infty}$ maximum appeared to be a linear combination of parameters describing the organic cosolvent.

The relative contribution of solvent basicity dominates over the contribution of the solvent acidity (Tab. 2, 3). The observed dependence is true for all analysed solvents (both single and mixed ones) and for all but $Bu_4NBr$ of the examined salts. This observation seems to point at the dominant role of cation solvation within the analysed set of solvents. The organic anion, that is hydrophobically hydrated in water and in water-organic mixtures does not change the observed sequence.

In the case of the transfer enthalpy of the salts from water to single organic solvents the increase of the organic cation size decreases the relative contribution of acid-base interactions in the total variation of the $\Delta_{tr}H^{\infty}$. The replacement of $Na^+$ or $K^+$ cation by an organic one reverses the sequence of acidity and basicity contributions.

The biggest contributions in the $\Delta_{tr}H^{\infty}$ variation within the set of the analysed organic solvents, for all investigated salts are given by (Tab. 2):

- $\pi^*$ - solvent polarizability/dipolarity, what was expected due to the presence of the ionic charge as well as the significance of the ion-dipole interactions,

- $\delta^2$(H) - cohesive energy density, as a parameter connected with the solvent structure change under influence of the ions, and including both the hydrogen bond contribution and the dipole-dipole interactions.

However, it should be noted that the statistical analysis method applied in this work makes it possible to determine the contributions of selected properties of the solvents to the total variation of the $\Delta_{tr}H^{\infty}$ values which are true only within a given set of solvents. The increase of number of examined solvents having different properties would somewhat change the calculation results. Unfortunately, the transfer enthalpies of electrolytes necessary for that analysis are known only for a limited number of single solvents and their mixtures with water.

REFERENCES

[1] G. M. Poltorackii, Termodinamicheskie kharakteristiki nievodnykh rastvorov elektrolitov, [Thermodynamic characteristics of nonaqueous electrolyte solutions], Khimiya, Leningrad 1984.

[2] I. A. Koppel, V. A. Palm, [in:] Advances in linear free energy relationships, Ed. by N. B. Chapman, J. Shorter, Plenum Publ. Co., New York 1972, Chapt. 5.

[3] T. M. Krygowski, W. R. Fawcett, J. Am. Chem. Soc., 97, 2143 (1975).

[4] W. R. Fawcett, T. M. Krygowski, Aust. J. Chem., 28, 2115 (1975).

[5] M. J. Kamlet, J.-L. M. Abboud, R. W. Taft, Prog. Phys. Org. Chem., 13, 485 (1981).

[6] M. H. Abraham, M. J. Kamlet, R. W. Taft, J. Chem. Soc., Perkin Trans. 2, 2, 923 (1982).

[7] M. J. Kamlet, J.-L. Abboud, M. H. Abraham, R. W. Taft, J. Org. Chem., 48, 2877 (1983).

[8] S. Taniewska-Osińska, B. Nowicka, A. Pietrzak, Thermochim. Acta, in press.

[9] Y. Marcus, Ion solvation, Ed. by Wiley, New York 1985.

[10] S. Taniewska-Osińska, A. Piekarska, A. Bald, A. Szejgis, Phys. Chem. Liq., 21, 217 (1990).

[11] S. Taniewska-Osińska, A. Piekarska, A. Bald, A. Szejgis, J. Chem. Soc. Faraday Trans. 1, 85, 3709 (1989).

Bożenna Nowicka, Henryk Piekarski

## WPŁYW WŁASNOŚCI ROZPUSZCZALNIKA NA ENTALPIĘ PRZENIESIENIA ELEKTROLITÓW Z WODY DO ROZPUSZCZALNIKÓW ORGANICZNYCH I MIESZANIN WODNO-ORGANICZNYCH

Entalpie przeniesienia ($\Delta_{tr}H^{\infty}$) elektrolitów z wody do szeregu rozpuszczalników organicznych zostały skorelowane z parametrami opisującymi wybrane własności rozpuszczalników. Przeanalizowano wpływ rodzaju i wielkości zarówno kationów, jak i anionów na względne udziały wybranych własności rozpuszczalnika w całkowitej zmienności $\Delta_{tr}H^{\infty}$ badanych soli. Analogiczne korelacje odnoszące się do entalpii przeniesienia soli z wody do mieszanin wodno-organicznych o składzie odpowiadającym maksimum $\Delta_{tr}H^{\infty}$ zostały również znalezione i przedyskutowane.