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THE TRANSFER ENERGIES OF HCl IN ETHYL UREA + WATER MIXTURES FROM ELECTROMOTIVE FORCE MEASUREMENTS BETWEEN 278.15 & 318.15 K.

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The transfer energies of hydrochloric acid in ethyl urea + water mixtures have been determined from electromotive force measurements of cells consisting of hydrogen and silver-silver chloride electrodes immersed in the mixed solvents containing the acid. Four different ethyl urea (EU) + water mixtures, involving 11.52, 20.31, 29.64 and 36.83 percentages by weight of EU, have been used. The molal concentration of the HCl solutions varied from 0.02 to 0.2 mole/Kg with respect to each solvent composition. The effect of temperature on the behavior of the system was also studied by measuring the cell potential at five different temperatures between 278.15 and 318.15 K. The free energy of HCl transfer decreased steadily with increasing the EU content of the mixed solvent. The entropy ($T\Delta S^\circ$) and enthalpy (ΔH°) of transfer increased rapidly to maximum values and then decreased as the mole fraction of EU in the mixture increased. The increase in $T\Delta S^\circ$ and ΔH° was ascribed to the formation of hydrogen-bonded EU + water complexes that are solvating the transferred ions. The structure enhancement in the mixed solvent was found to be more pronounced as compared with such mixed solvents as aqueous urea or methyl urea.

يتناول موضوع البحث ايجاد طاقات الانتقال لكلوريد الهيدروجين في مزيجات اليوريا مع الماء من قياسات القوة الدافعة الكهربية لخللا لا تشمل على الانتقال. وكان قطبا الخلية من الهيدروجين والفضة المغطى بكلوريد الفضة المعتمدين في المزيج الذي اضيف اليه حامض الهيدروكلوريك. استخدمت اربعة تراكيب مختلفة من المذيب اشتملت على 11.52، 20.31، 29.64 و 36.83٪ وزنا من اثيل اليوريا في الماء. وتراوحت التراكيب المولالية للحامض من 0.02 الى 0.2 مول لكل كيلوغرام من المذيب. وجرت القياسات في خمسة درجات حرارية في المدى 278.15 و 318.15 كلفن. قلت الطاقة الحرة لانتقال حامض HCl بصورة منتظمة مع ازدياد مقدار اثيل اليوريا في المزيج. وبالمقابل ازادت قيم انتروبي وانتالي الانتقال الى قيم قصوى ثم قلت ثانية مع ازدياد الكسر المولي لايثيل اليوريا في المزيج. وعزيت الزيادة في الانتروبي والانتالي الى تكوين معقدات خاصة نتيجة الانتقال.

INTRODUCTION

There have been a number of investigations on the transfer energy determination of HCl in urea + water mixtures from electromotive force measurements of cells without transference¹⁻³. Little direct information is so far available concerning the transfer energies of HCl in aqueous n-alkyl ureas despite the significance of such data for a deeper understanding of the behaviour of HCl in aqueous urea.

In a previous paper⁴, we have examined the behaviour of HCl in n-methyl urea + water mixtures by which some information was gained regarding the influence of the methyl group of the urea compound on the thermodynamic properties of the electrolyte. The present paper is an attempt to expand the previous studies using ethyl urea or urea mixtures with water in order to find out the extent of the variations in the thermodynamic properties of HCl as a consequence of the ethyl group of the urea compound.

EXPERIMENTAL

The apparatus and the general technique employed in this investigation have already been described as have the preparation of the hydrogen and the silver-silver chloride electrodes and their arrangements in the cell³⁻⁵. Ethyl urea (EU) was a pure (>99%) sample obtained from Fluka and it was further purified before use.

The density (d_s) of the solvent mixture was determined with a pycnometer, of 25 ml capacity, which was correct to within 0.01 mg cm⁻³. The dielectric constant (ϵ_s) of the solvent was measured by a Universal Dielectrometer; the error in any reading was less than 1%. Table 1 shows the values of d_s and ϵ_s at five different temperatures, which were utilized for the evaluation of some necessary constants³⁻⁵.

Table 1- The densities (d_s), in g cm⁻³, and the dielectric constant (ϵ_s): $T_1 = 278.15$ K, $T_2 = 288.15$ K, $T_3 = 298.15$ K, $T_4 = 308$ K and $T_5 = 318.15$ K. The average molecular weight (M_s) of the solvent mixtures, the percentages by weight (W,%) of the EU in the mixtures are given for four different EU + water composition.

| | | X = 0.025 | | | and $M_s = 19.816$ | |
|------------------------------|--------------|------------|--------|--------|--------------------|--------|
| | | T_1 | T_2 | T_3 | T_4 | T_5 |
| A) 11.52% = W ₁ % | d_s | 1.0191 | 1.0178 | 1.0133 | 1.0119 | 1.0108 |
| | ϵ_s | 87.04 | 84.54 | 80.76 | 76.93 | 72.82 |
| | | X = 0.0496 | | | and $M_s = 21.469$ | |
| | | T_1 | T_2 | T_3 | T_4 | T_5 |
| B) 20.31% = W ₁ % | d_s | 1.0267 | 1.0255 | 1.0234 | 1.0220 | 1.0202 |
| | ϵ_s | 93.15 | 87.08 | 81.48 | 77.29 | 73.06 |
| | | X = 0.0793 | | | and $M_s = 23.555$ | |
| | | T_1 | T_2 | T_3 | T_4 | T_5 |
| C) 29.64% = W ₁ % | d_s | 1.0397 | 1.0361 | 1.0342 | 1.0323 | 1.0309 |
| | ϵ_s | 94.03 | 88.91 | 83.42 | 77.60 | 73.89 |
| | | X = 0.1066 | | | and $M_s = 25.461$ | |
| | | T_1 | T_2 | T_3 | T_4 | T_5 |
| D) 36.83% = W ₁ % | d_s | 1.0503 | 1.0455 | 1.0433 | 1.0407 | 1.0374 |
| | ϵ_s | 95.65 | 89.16 | 83.79 | 78.72 | 74.60 |

RESULTS

The e.m.f. (E) of the cell:
 $\text{Pt, H}_2(\text{g, 1 atm}) \text{HCl}(\text{m}), \text{ethyl urea} + \text{water mix; AgCl}(\text{s}), \text{Ag}$

have been measured for four different urea (EU) + water mixtures involving 11.52, 20.31, 29.64 and 36.83 percentages by weight of EU respectively. The molal concentration (m) of the HCl solutions varied from about 0.02 to 0.2 mole Kg⁻¹ with respect to each solvent mixture. The effect of temperature on the behaviour of the system was also investigated by determining the cell voltage at five different temperatures: 278.15, 288.15, 308.15 and 318.15 K. The experimental results of such measurements are given in table 2.

Table 2- The electromotive force (E) of the cell at different molal concentrations (m) of HCl with respect to each of the solvent compositions (W,%).

| W, % ethyl urea | m / mol kg ⁻¹ | E (volt) at temperature / K | | | | |
|--------------------|-----------------------------|-----------------------------|--------|--------|--------|--------|
| | | 278.15 | 288.15 | 298.15 | 308.15 | 318.15 |
| 11.52 | 0.0200 | 0.4570 | 0.4645 | 0.4685 | 0.4755 | 0.4775 |
| | 0.0400 | 0.4330 | 0.4380 | 0.4415 | 0.4450 | 0.4460 |
| | 0.0600 | 0.4160 | 0.4210 | 0.4255 | 0.4265 | 0.4275 |
| | 0.0800 | 0.4030 | 0.4080 | 0.4091 | 0.4130 | 0.4155 |
| | 0.1000 | 0.3935 | 0.3970 | 0.3985 | 0.3996 | 0.4000 |
| | 0.2007 | 0.3610 | 0.3630 | 0.3665 | 0.3675 | 0.3695 |
| | 20.31 | 0.0200 | 0.4590 | 0.4676 | 0.4785 | 0.4845 |
| 0.0400 | | 0.4360 | 0.4445 | 0.4486 | 0.4555 | 0.4594 |
| 0.0600 | | 0.4170 | 0.4235 | 0.4300 | 0.4360 | 0.4370 |
| 0.0800 | | 0.4010 | 0.4095 | 0.4165 | 0.4175 | 0.4180 |
| 0.1000 | | 0.3975 | 0.4060 | 0.4085 | 0.4090 | 0.4095 |
| 0.2007 | | 0.3640 | 0.3710 | 0.3715 | 0.3730 | 0.3735 |
| 29.64 | | 0.0200 | 0.4710 | 0.4835 | 0.4876 | 0.4925 |
| | 0.0400 | 0.4405 | 0.4480 | 0.4565 | 0.4575 | 0.4580 |
| | 0.0600 | 0.4225 | 0.4320 | 0.4340 | 0.4395 | 0.4420 |
| | 0.0800 | 0.4155 | 0.4180 | 0.4255 | 0.4270 | 0.4275 |
| | 0.1000 | 0.4065 | 0.4110 | 0.4130 | 0.4145 | 0.4150 |
| | 0.2007 | 0.3780 | 0.3820 | 0.3825 | 0.3838 | 0.3850 |
| | 36.83 | 0.0200 | 0.4751 | 0.4861 | 0.4876 | 0.5056 |
| 0.0400 | | 0.4435 | 0.4515 | 0.4600 | 0.4640 | 0.4660 |
| 0.0600 | | 0.4330 | 0.4390 | 0.4435 | 0.4455 | 0.4475 |
| 0.0800 | | 0.4175 | 0.4195 | 0.4230 | 0.4265 | 0.4305 |
| 0.1000 | | 0.4080 | 0.4165 | 0.4189 | 0.4210 | 0.4210 |
| 0.2007 | | 0.3805 | 0.3809 | 0.3860 | 0.3876 | 0.3890 |

The Standard Potentials

The e.m.f. (E) of the cell for any molality (m) of HCl is related to the standard potential of the cell (E°_m) by eqn. (1):

$$E = E^{\circ}_m - 2k \log m - 2k \log \gamma_{\pm} \quad (1)$$

where γ_{\pm} is the mean molal activity coefficient of HCl and $k = 2.303 RT/F$.

The values of E° at different temperatures and solvent compositions are then determined by similar calculations to those adopted earlier^{1,3-5} and the results are given in table 3. The temperature dependence of E° values could be expressed as:⁽¹⁻⁵⁾

Table 3- The standard potential of the cell on the molal scale (E°_m) at different temperatures and solvent compositions.

| W ₁ % | E° (volt) at temperature /K. | | | | |
|------------------|---------------------------------------|--------|--------|--------|--------|
| ethyl urea | 278.15 | 288.15 | 298.15 | 308.15 | 318.15 |
| 11.52 | 0.2676 | 0.2677 | 0.2659 | 0.2640 | 0.2599 |
| 20.31 | 0.2694 | 0.2709 | 0.2733 | 0.2720 | 0.2674 |
| 29.64 | 0.2766 | 0.2799 | 0.2811 | 0.2777 | 0.2721 |
| 36.83 | 0.2820 | 0.2849 | 0.2846 | 0.2841 | 0.2840 |

$$E^{\circ}_m = a + b(t-25) + c(t-25)^2 \quad (2)$$

where T is the temperature ($^{\circ}\text{C}$). The constants a, b and c for the different solvent mixtures, obtained by the least square method, are given in table 4.

Table 4- The temperature dependence of E° for various solvent compositions.

| W% ethyl urea | a /volt | $bx10^4$ /volt deg | $-cx10^6$ / (volt deg) ² |
|---------------|---------|--------------------|-------------------------------------|
| 0.00 | 0.2224 | 6.3964 | 3.1810 |
| 11.52 | 0.2672 | 1.1257 | 6.0714 |
| 20.31 | 0.2699 | 2.4438 | 6.3771 |
| 29.64 | 0.2734 | 6.8285 | 15.8571 |
| 36.83 | 0.2798 | 4.260 | 7.000 |

The values of E_m° of table 3 have then been used to calculate the standard potentials of the cell on the molar (E_c°) and the mole fraction (E_N°) scales by the equations:

$$E_c^{\circ} = E_m^{\circ} + 2k \log d_s \quad (3)$$

and

$$E_N^{\circ} = E_m^{\circ} - 2k \log (1000/M_s) \quad (4)$$

where d_s and M_s represent the density and average molecular weight of the solvent mixtures respectively; the data thus obtained for various solvent compositions are shown in table 5.

Table 5 - The standard potential of the cell on the molar (E_c°) and mole fraction (E_N°) scales, in volt, for various solvent compositions at 298.15 K.

| W _{ethyl urea} | E_c° | E_N° |
|-------------------------|---------------|---------------|
| 0.00 | 0.2216 | 0.0160 |
| 11.52 | 0.2665 | 0.0644 |
| 20.31 | 0.2744 | 0.0759 |
| 29.64 | 0.2828 | 0.0884 |
| 36.83 | 0.2867 | 0.0959 |

The Transfer Energies

The standard free energy changes ΔG° , accompanying the transfer of one mole of HCl from water to each of the solvent mixtures were estimated from the difference in the values of (E_N°)_s (table 5) for water ($(E_N^{\circ})_w$) and the solvent mixture ($(E_N^{\circ})_s$) using the relation (5):

$$\Delta G^{\circ} = -F [(E_N^{\circ})_s - (E_N^{\circ})_w] \quad (5)$$

The mole fraction scale has been used in order to eliminate the effects arising from the concentration changes of HCl which accompany the transfer process and to reflect the solvent effect more clearly, a contention that has been shown to be true for many other solvent mixtures⁶. Assuming that E values in water and the solvent mixtures are accurate to within ± 0.02 mV the probable uncertainties in ΔG° values will lie within ± 33 J/mole.

The corresponding changes in the standard entropy of the transfer ΔS_t° were calculated from the molecular weights of water (M_w) and the solvent mixture (M_s) and the temperature dependence constant (b) of E_m° (table 4) for water (b_w) and the solvent (b_s) using the relationship:

$$\Delta S_t^\circ = (b_s - b_w) - (2 \times 2.303 R/F) \log (M_w/M_s) \quad (6)$$

it was also possible to estimate the standard enthalpy of transfer (ΔH_t°) from the values of ΔG_t° and ΔS_t° at a constant temperature. The transfer energies against composition profiles at 298.15K are illustrated in figures 1,2 and 3. The previous results with urea and n-methyl urease have also been inserted in the figures for composition.

The Electrstatic and Chemical Contributions

The transfer energy consists of two parts: the electrstatic (el) and the chemical (ch) or also called the non-electrstatic. the former effects arise from the change in the dielectric constant (ϵ) of the medium, whereas, the chemical contribution reflects the solvating capacity as well as the specific chemical interactions, which involves the destruction of one type of solvation shell and the creation of another.

An attempt was made to find the electrstatic contributions, $\Delta G_{t,el}^\circ$, $\Delta S_{t,el}^\circ$ to the total standard free energy ΔG_t° and entrpny ΔS_t° of transfer using Born model^{3-5,7}. The effective radius of the hydronium ion was taken as 2.76 Å while that of the chloride was considered 1.817 Å⁽¹⁾. The constants characteristics of the medium in Born model were estimated from the plots of $\log \epsilon$ values versus the temperature as before³⁻⁵. The values of $\Delta G_{t,el}^\circ$ and $\Delta S_{t,el}^\circ$ were then used to determine the chemical contribution to the free energy ($\Delta G_{t,ch}^\circ$) and to the entrpny ($\Delta S_{t,ch}^\circ$) of the transfer; the data obtained are given in table 6. The electrstatic and the chemical contributions to the enthalpy of transfer, which were calculated from the corresponding free energy and entrpny of transfer at a constant temperature, have also inserted in table 6.

Table 6 - The electrstatic (el) and the chemical (ch) contributions to the free energy, enthalpy (in k J mol⁻¹) and entrpny (in J mol⁻¹ deg⁻¹) of transfer for HCl at 298.15 K and different solvent compositions.

| W ₁ % ethyl urea | ΔG_t° | | ΔS_t° | | ΔH_t° | |
|-----------------------------|--------------------|--------|--------------------|---------|--------------------|--------|
| | el | ch | el | ch | el | ch |
| 11.52 | -0.2224 | -4.419 | -5.274 | 79.441 | -1.794 | 19.264 |
| 20.31 | -0.2919 | -5.462 | -15.759 | 103.933 | -4.990 | 25.538 |
| 29.64 | -0.4733 | -6.492 | -8.642 | 140.712 | -3.049 | 35.459 |
| 36.83 | -0.5069 | -7.435 | -7.435 | 116.015 | 2.723 | 27.407 |

Free Energy of Transfer

The results of fig.1 show a steady decrease of ΔG° , with increasing mole fraction (X) of the ethyl urea in the solvent mixtures. The contribution of $\Delta G^\circ_{t,el}$, as indicated in table 6, was far less than of $\Delta G^\circ_{t,ch}$ in lowering the standard free energy of transfer in ethyl urea + water mixtures. The lowering of ΔG° , at $X < 0.039$, as shown in fig.1, was more extensive in aqueous ethyl urea as compared with the results in aqueous urea or methyl urea. Beyond such a mole fraction value ($X=0.039$), aqueous urea becomes more influential in lowering the ΔG° , values of HCl than the other two aqueous ureas. The three ureas could then be arranged, on the basis of their capacity to decrease the free energy of HCl transfer, as:

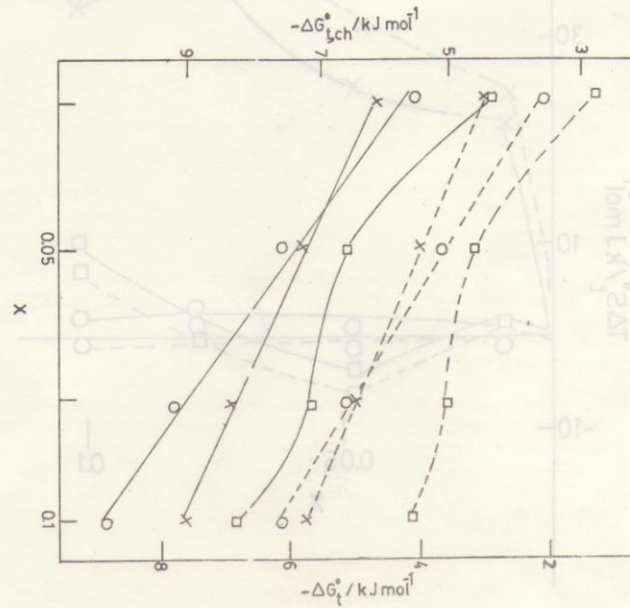


Fig.1 The standard free energy of HCl transfer (ΔG°) at 298.15 K plotted against the mole fraction (X) of the urea compound in the mixed solvents. The corresponding chemical contributions to the free energy of transfer ($\Delta G^\circ_{t,ch}$) against X are indicated in the dotted lines. Urea (□) : ethyl urea (x)

The results of fig. 1 show a steady decrease of ΔG° with increasing mole fraction (X) of the ethyl urea in the solvent mixture. The contribution of ΔG°_{ch} as indicated in table 6 was far less than of ΔG°_{tr} in lowering the standard free energy of transfer in ethyl urea + water mixtures. The lowering of ΔG° at $X < 0.030$, as shown in fig. 1, was more extensive in respect to ethyl urea as compared with the results in aqueous urea or methyl urea. Beyond a mole fraction value ($X=0.030$), aqueous urea becomes more influential than ethyl urea in lowering the ΔG° values of HCl than the other two aqueous ureas. The three ureas are ranked, on the basis of their capacity to decrease the free energy of transfer.

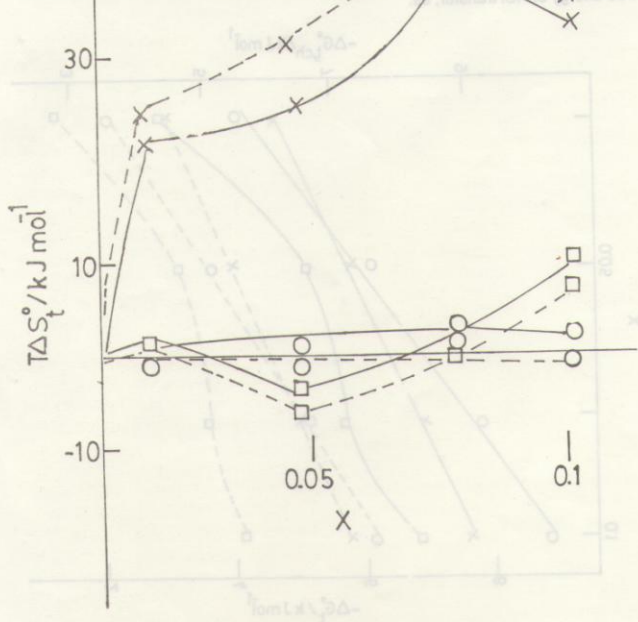


Fig. 2 Variation of $T\Delta S^\ddagger$ for HCl in the mixed solvents at 298.15 K against X. The lines correspond to the chemical contributions to the entropy of transfer ($T\Delta S_{ch}$). The symbols as in fig. 1.

urea > ethyl urea > methyl urea ———(a)

The hydrophobicity of the three ureas in an aqueous medium is known to follow the sequence⁸⁻¹⁰:

ethyl urea > methyl urea > urea ———(b)

Such a sequence arises possibly due to the greater effective surface area of the ethyl group as compared with the methyl group of methyl urea and consequently the specific interaction of urea with the surrounding water molecules should exceed that of the methyl urea and the least interaction tendency with water should be shown by the ethyl urea.

Urea with least hydrophobicity, as compared with the other two ureas in the sequence b, should show more power in water structure destruction and for the solvation of hydrogen ions. This expectation agrees with the experimental results in fig. 1, where the aqueous urea occupies the extreme position on the left of the sequence a. The behaviour of ethyl urea against the hydrophobicity trend, as compared with methyl urea, may be a consequence of the greater inductive effect of the ethyl group than of the methyl group resulting possibly in a more basic property in the former case as compared with latter. Moreover, the electron donating tendency of the methyl group may account for the exceptionally higher capacity of aqueous ethyl urea for ΔG° , lowering of HCl at $X < 0.039$. The hydrophobicity factor predominates on the electron donating capacity as X increases and hence making aqueous urea more effective than aqueous ethyl urea.

Entropy and Enthalpy Changes

The entropy and enthalpy changes, as shown in figures 2 and 3, may be taken as a measure for the alterations that take place in the structure of the solvent mixtures. The variations in $T\Delta S^\circ_{\text{sch}}$ with X (fig.2) were substantial and occurred in a similar manner to those in $T\Delta S^\circ$. This suggests that the variations in ΔS° with the composition of the solvent are mainly of chemical nature.^b

Three distinct parts are indicated on each plot of figures 2 and 3 with regard to ethyl urea + water mixtures. There is an initial rapid increase of $T\Delta S^\circ$ (also of $T\Delta S^\circ_{\text{sch}}$) and ΔH° with X in the first part which continues until X is 0.024. This is followed by a slower increase in these thermodynamic quantities attaining their maxima at $X = 0.0793$. The third part of the plot in figures 2 and 3 involves a steady decrease of $T\Delta S^\circ$ and ΔH° , just after exceeding $X = 0.0793$.

The initial rapid increase of $T\Delta S^\circ$ in the first part may arise as a consequence of a rapid enhancement in the structure of the solvent due probably to the formation of the hydrogen-bonded ethyl urea + water complexes which solvate the hydrogen ions. The slower increase of the thermodynamic quantities ($T\Delta S^\circ$ and ΔH°) with X in the second part of the plots corresponds possibly to a slower completion of the solvent structure and the subsequent ion solvation. A part of the added ethyl urea may participate in the already formed solvent structures. In the mean time, some of non-interacting or

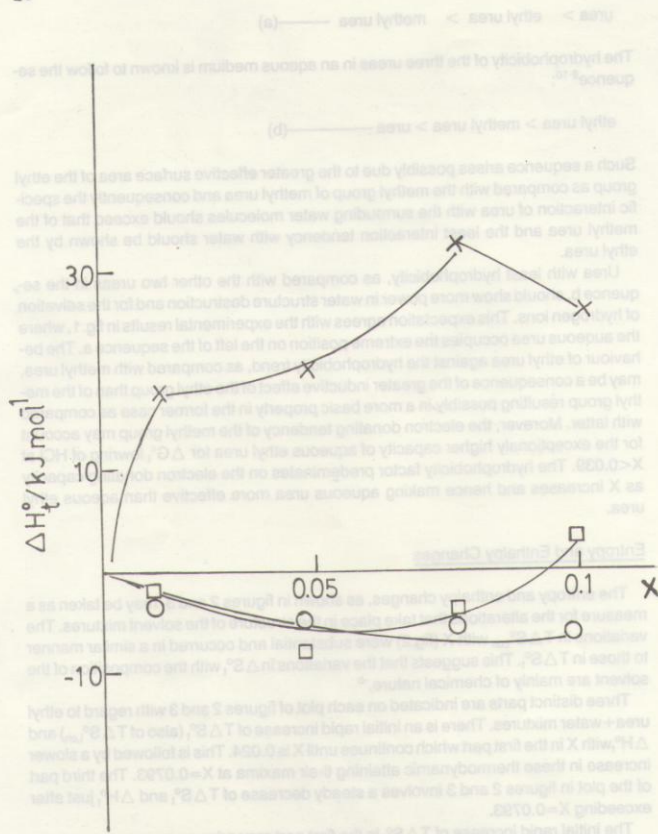


Fig.3. The standard enthalpy of HCl transfer (ΔH°) in the mixed solvents, at 298.15K, plotted against X.

loosely bound water molecules in the solvent structure may take part in the structure formation with the newly added ethyl urea. The net change in $T\Delta S^\circ$ and ΔH° in such processes are expected to be less per unit ethyl urea concentration and requiring less water structure destruction as compared with the process in the first part.

The third part of the plots (figs. 2 and 3) showing a steady decrease of $T\Delta S^\circ$ and ΔH° with increasing X corresponds probably to a steady and slow destruction of the solvent structure as well as of the water aggregates around the lyophobic ethyl groups of the area compound. Water molecules may now be needed^{11,12} to interact with the newly added ethyl urea and these are possibly obtained by partial destruction of the existing complexes. This may allow for a new arrangement in the solvent complexation corresponding to smaller entropy and enthalpy changes than for building up of structure in the processes represented by the first two parts of the plots.

No such drastic alterations occurred in $T\Delta S^\circ$ and ΔH° when HCl was solvated in aqueous urea or methyl urea (fig.2 and 3). In the case of aqueous urea, there was a steady but slight changes as X increased. The structure formation in aqueous methyl urea was

more pronounced than of urea but far less considerable than of aqueous ethyl urea. The enhancement of structure in methyl urea + water mixture came to completion at $X=0.024$ which, thereafter, underwent destruction steadily. This was followed by a new increase in $T\Delta S^\circ$ and ΔH° corresponding to a new enhancement in structure. The structure enhancement in the mixed solvent was generally far more substantial in aqueous ethyl urea as compared with aqueous urea or aqueous methyl urea. This is again an indication for a greater solvating capacity of the ethyl urea + water complex over a certain range of concentrations than the mixed solvent of the other two ureas. such a capacity may also be attributed to the higher electro-donating power of the ethyl group of ethyl urea.

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