ACTA UNIVERSITATIS LODZIENSIS
FOLIA CHIMICA 1, 1982

Stefania Taniewska-Osińska, Alina Piekarska

THERMOCHEMICAL INVESTIGATIONS OF NaI-WATER-ISOPROPANOL SYSTEM WITH ADDITION OF FORMAMIDE AND OF N,N-DIMETHYLFORMAMIDE AT TEMPERATURE 298.16 K

Enthalpy of solution of NaI in water - isopropanol mixtures with the addition of formamide and of N,N-dimethylformamide was measured. The course of relation of standard enthalpy of NaI solution in the investigated mixed solvents vs. alcohol and amide contents was discussed.

The mixtures of DMF with water have already been investigated several times by different experimental methods. Yet, there is no unanimity in the opinions about the influence of DMF on water structure. Some authors e.g. K e s s l e r [1, 2] S z a p c h a r o n o w [3] claim that DMF exerts ordering influence on water structure while others [4, 5] on the contrary are of the opinion that DMF breaks water structure.

Recently we have carried out thermochemical [6] densimetric and viscosimetric [7] investigations of NaI solutions in the mixtures of formamide and of N,N-dimethylformamide with water. The results obtained by us point to certain differences between formamide - water and DMF - water interactions but in our opinion N,N-dimethylformamide, alike formamide destroys the threedimensional water structure. As the result, strong mixed associates are formed which according to some authors [1, 2] is the manifestation of structure ordering.

In order to find one more argument concerning the influence

of DMF on water structure we have carried out additional investigations.

Experimental

Sodium iodide p. a. (Merck, Germany) was crystallized from the mixture of acetone and water in a 1:1 ratio (by volume) and dried in a vacuum dryer at ca 343 K.

Formamide-puriss (Merck, Germany) was dried using CaO and then distilled twice under a pressure of 1 mm Hg.

N,N-dimethylformamide for spectroscopy (Fluk A. G.) was dried over molecular sieves type 4A and twice distilled under a pressure of 3.7 mm Hg. Isopropanol p. a. (P. O. Ch., Gliwice, Poland) was dried by the Lund-Bjerrum method [8]. Contaminations determined by gas chromatography (Perkin-Elmer F-11) did not exceed a total of 0.05%. Water was demineralized using ion exchangers and then twice distilled. The solutions were prepared by weight. The measurements were made in a calorimeter described previously [9].

Results and discussion

We have measured NaI solution enthalpy in water - isopropanol - N,N-dimethylformamide and water - isopropanol - formamide mixtures with different composition at temp. 298.16 K. The range of electrolyte concentrations was from 0.003 to 0.05 mol NaI/kg of the mixed solvent. Basing on the obtained data we have determined the values of NaI standard solution enthalpy (ΔH^{o}) in all investigated mixtures using the method of graphical extrapolation of the function $\Delta H_m = f(\sqrt{m})$. The obtained results are presented in Fig. 1 and 2.

It follows from the presented results that the effect of the added alcohol on the structure of NaI solutions in water - N,N-dimethylformamide mixture is different than the effect of DMF on the structure of NaI solutions in water-alcohol mixtures.

In the first case (Fig. 1a) the increase of alcohol content in all investigated DMF with water mixed solvent causes at first the increase of solution enthalpy (lowering of solution heat exotermicity) and then its decrease. On the curves of the relation $\Delta H^{\circ} = f(x_{alc})$ maximum can be observed which decreases with the growth of N,N-dimethylformamide content and shifts towards lower isopropyl alcohol contents in the mixture.

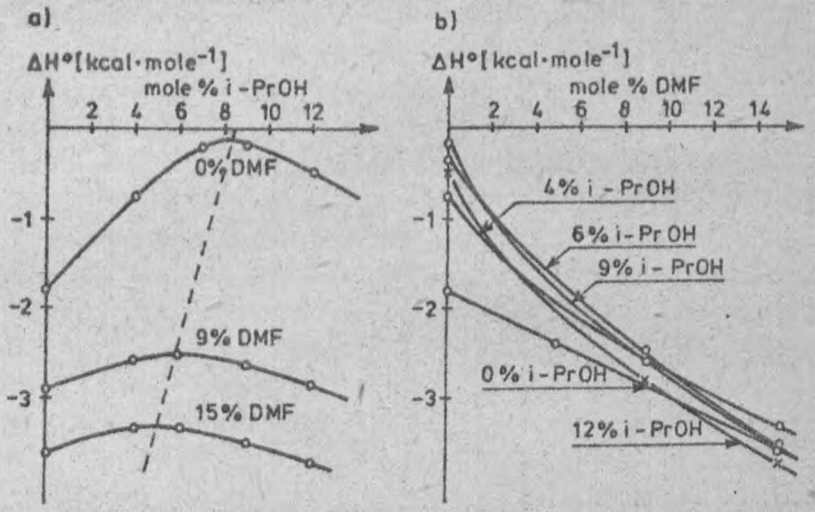

Fig. 1. The standard dissolution enthalpy of NaI in water-isopropanol-N,N-dimethylformamide system as a function of isopropanol (a) and N,N-dimethylformamide (b) content

In the second case (Fig. 1b) the growth of DMF content in all investigated mixtures of isopropyl alcohol with water causes decrease of NaI dissolution enthalpy (on the curves of $\Delta H^{\circ} = f(x_{DMF})$ relation no maximum is observed).

The first portions of DMF cause more distinct changes of the course of the function $\Delta H^{\circ} = f(x_{DMF})$ than the next ones. It can be also observed that the higher isopropanol content in the mixture with water the more rapid increase of exothermicity of NaI heat effect caused by the addition of dimethylformamide. In such a case the character of the curves $\Delta H^{\circ} = f(x_{alc})$ and $\Delta H^{\circ} = f(x_{DMF})$ differs, which is probably connected with different effect of monohydric alcohols and DMF on water structure. Small ammounts of isopropyl alcohol stabilize water structure destro-

yed by dimethylformamide. Next portions of alcohol cause the destruction of water structure. With the increase of DMF contents this effect decreases which is pointed out by the lowering of maximum on the curves of $\Delta H^{o} = f(x_{alc})$ relation.

On the other hand the addition of DMF to isopropyl alcohol--water mixture causes the breaking of water structure previously strengthened by alcohol. Analogous conclusions can be drawn from the results of the investigations of water - formamide - isopropyl alcohol - NaI system carried out by us (Fig. 2).

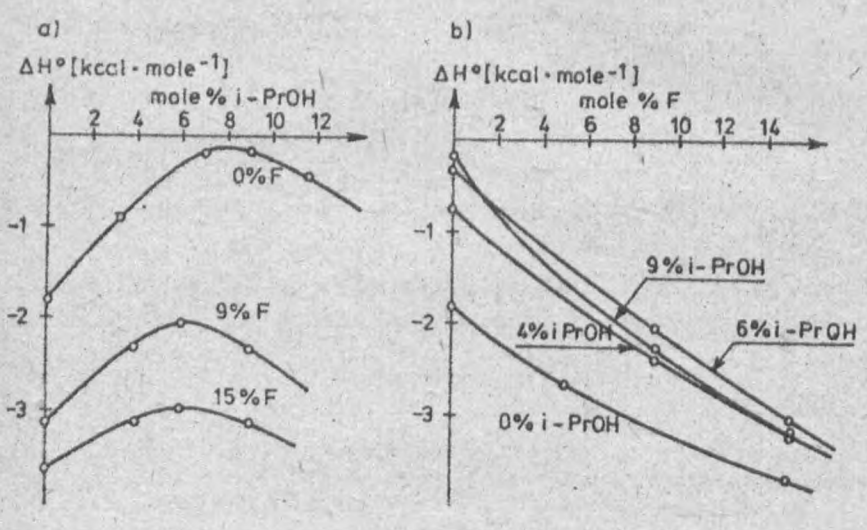

Fig. 2. The standard dissolution enthalpy of NaI in water-isopropanol-formamide system as a function of isopropanol (a) and formamide (b) content

It is known that formamide is one of water structure breaking substances [10-13]. The course of curves of NaI enthalpies as a function of alcohol and formamide content in this system is analogous to the course of ΔH^{o} curves in the previously discussed water - DMF - isopropyl alcohol - NaI system. This indicates that the behaviour of DMF is similar to that of formamide.

The results of our investigations seem to point to the fact that both investigated amides break the threedimensional water structure.

REFERENCES

[1] Mishustin A. I., Kessler Yu. M., Zhur. Strukt. Khim., 15, 205 (1974).
[2] Verstakov E. S., Yastremskii P. S., Kessler Yu. M., Mishustin A. I., Emelin V. P., Zhur. Fiz. Khim., 49, 1604 (1975).
[3] Shakhparonov M. I., Raikhe B., Lanshina L. V., Fizika i fizikokhimiya zhydkostei, Moskva (1973).
[4] Fratiello A., Molec. Phys., 7, 565 (1963-1964).
[5] Grochowski R., Thesis University of Lódź, Lódź (1971).
[6] Taniewska-Osińska S., Piekarska A., Bull. Acad. Polon. Sci. Ser. Sci. Chim., 26, 601, 613 (1978).
[7] Piekarska A., Thesis University of Lódź, Lódź (1976).
[8] Lund H., Bjerrum J., Ber., 64, 210 (1931).
[9] Taniewska-Osińska S., Piekarski H., J. Solut. Chemistry 7, 891 (1978).
[10] Kessler Yu. M., Emelin V. P., Tolubeev Yu. S., Truskov O. V., Lapshin R. M., Zhur. Strukt. Khim., 13, 211 (1972).
[11] Sunner S., Canad. J. Chem., 38, 681 (1960).
[12] Yastremskii P. S., Verstakov E. S., Kessler Yu. M., Mishustin A. I., Emelin V. P., Bobrinev Yu. M., Zhur. Fiz. Khim., 49, 2950 (1975).
[13] Rohdewald P., Moldner M., J. Phys. Chem., 77, 373 (1973).

Department of Physical Chemistry
Institute of Chemistry
University of Łódź

Stefania Taniewska-Osińska, Alina Piekarska

TERMOCHEMICZNE BADANIA UKŁADU NaI-WODA-IZOPROPANOL Z DODATKIEM FORMAMIDU I N,N-DWUMETYLOFORMAMIDU W TEMPERATURZE 298,16 K

Zmierzono entalpię rozpuszczania NaI w mieszaninach wody z izopropanolem z dodatkami formamidu i N,N-dwumetyloformamidu w temp. 298,16 K. Stężenie elektrolitu wynosiło od 0.003 do 0.05 mola NaI/kg rozpuszczalnika mieszanego.

Na podstawie uzyskanych danych wyznaczono wartości standardowej entalpii rozpuszczania (ΔH°). NaI we wszystkich badanych mieszaninach. Analiza uzyskanych wyników wykazała, że wpływ dodanego alkoholu na strukturę mieszaniny woda-DMF jest odmienny niż wpływ DMF na strukturę mieszanin woda - alkohol. Niewielkie ilości alkoholu izopropylowego stabilizują zniszczoną przez DMF strukturę wody. Dalsze porcje alkoholu powodują niszczenie struktury wody. Ze wzrostem zawartości DMF efekt staje się mniejszy, o czym świadczy obniżenie wysokości maksimum na krzywych zależności $\Delta H^\circ = f(x \text{ alcohol})$. Z drugiej strony dodatek DMF do mieszaniny izopropanol-woda powoduje niszczenie wzmocnionej uprzednio alkoholem struktury wody.

Analogiczne wnioski można wysnuć na podstawie wyników przeprowadzonych przez nas badań układu: woda - formamid - alkohol izopropylowy - NaI.

Стефания Таневска-Осиньска, Алина Пекарска

ТЕРМОХИМИЯ СИСТЕМ NaI ВОДА-ИЗОПРОПАНОЛ С ДОБАВКАМИ ФОРМАМИДА И ДМФ ПРИ 298,16 К

Измерена энтальпия растворения NaI в смесях вода-изопропанол с добавками формамида и ДМФ при температуре 298,16 К. Концентрационный интервал по электролиту составил 0,003-0,05 моль NaI/кг растворителя. Измеренные значения энтальпии растворения NaI во всех изученных смесях экстраполировалось до бесконечно большого разведения (ΔH°). Анализ полученных результатов сказывает, что действие добавок спирта на структуру смесей вода-диметилформамид и добавок ДМФ на структуру смесей вода-изопропиловый спирт неодинаково. Небольшие добавки изопропилового спирта стабилизируют разрушенную Н, Н-диметилоформамидом структуру воды, а затем ее разрушают. С повышением концентрации ДМФ этот эффект выражен в меньшей степени, о чем свидетельствует снижение высоты максимума на кривых зависимости $\Delta H^\circ = f(x \text{ сп.})$. Добавка ДМФ к системе изопропиловый спирт-вода вызывают разрушение упрочнунной спиртом структуры воды. Аналогичные результаты получены для системы вода-формамид - изопропиловый спирт - NaI.