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CALORIMETRIC INVESTIGATION OF ANILINE SOLUTIONS IN HMPT-H_2O MIXTURES AT 298.15 K

Enthalpies of solution of aniline, KI and KCl in **HMPT-water mixtures** containing up to 3 mole % of HMPT **were measured.** Standard enthalpies of solution ΔH^{o} and enthalpies of transfer of the compounds under study from water to the mixed solvent ΔH^{o}_{tr} were calculated. The results obtained experimentally are extensively discussed against the background of the relevant literature data.

Introduction

In view of the fact that hexamethylphosphoramide (HMPT) is an aprotic solvent with good dissolving properties relative to a wide range of both electrolytes and organic substances the compound has received a lot of attention of investigators. Mixtures of HMPT with water have been studied by spectroscopic [1-3] as well as by densimetric, viscosimetric, and conductometric [4-8] methods. Similarly, three-component HMPT-H_2O-electrolyte mixtures have been studied by densimetric, viscosimetric, and conductometric methods [4-8] as well as calorimetrically [9].

An analysis of the results obtained led Kessler to the conclusion that HMPT forms clatrates with water [1-3]. Merlin et al. [10] investigated three-component HMPT-H_2O-nonelectrolyte mixtures and, on the basis of studies of ΔG^{o}_{tr}, ΔH^{o}_{tr}, and ΔS^{o}_{tr}, they suggested that HMPT might be regarded as a hydrophobic compound with structure making properties relative to water in water-rich mixtures. Between hydrophobic compounds on the one hand, and HMPT on the other, there may place intermiscibility or interggregation. The aim of the research reported here was to obtain more information about HMPT-H_2O system by way of calorimetric measurements of the heat of solution of a third substance in it. Aniline was selected as the solute and its heat of dissolution was determined in the range of small HMPT contents, the range that seems particularly interesting in light of the research referred to above.

Experimental

Pure HMPT manufactured by FIuka AG with water content of less than 0.05 per cent and n_d of 1.459 was employed. Aniline, dried over KOH, was distilled prior to each measurement; its purity was tested by UV and IR spectroscopy. The measurements were made in an ""isoperibol" type calorimeter at 298.15 ± 0.005 K. The heat of aniline solution was measured in the range of 0.0043-0.0221 mole/kg in the mixed solvent which contained from 0 to 3 mole per cent of HMPT in water.

Results and discussion

The heats of aniline solution in water and in the mixed solvent HMPT + H_2O, and the heat of aniline transfer to the mixed solvent are presented in Tab. 1.

Standard enthalpies of solution in infinitely dilute solutions ΔH^o for aniline dissolved in water and in the mixed solvent HMPT + H_2O have been determined graphically. The heats of aniline transfer from water to the mixed solvent are plotted in Fig. 1, together with the corresponding function obtained for p-nitroaniline by Merlin et al. [10] who calculated the enthalpy of transfer taking advantage of solubility measurements and using the formula:

Table 1

Heat of solution of $C_6H_5NH_2$ in water-HMPT mixtures at 298.15 K

x_{HMPT}	$m_{C_6H_5NH_2}$ [mol/kg]	ΔH [J/mol]	ΔH^o_{tr} [J/mol]	x_{HMPT}	$m_{C_6H_5NH_2}$ [mol/kg]	ΔH [J/mol]	ΔH^o_{tr} [J/mol]	x_{HMPT}	$m_{C_6H_5NH_2}$ [mol/kg]	ΔH [J/mol]	ΔH^o_{tr} [J/mol]
0.0000	0.0062	1816	0	0.0051	0.0047	3628	-1791	0.0201	0.0048	8460	-6640
	0.0069	1807			0.0048	3607			0.0050	8443	
	0.0072	1820			0.0080	3586			0.0097	8439	
	0.0072	1812			0.0088	3586			0.0100	8439	
	0.0073	1833			0.0185	3565			0.0182	8414	
	0.0073	1833			0.0208	3569			0.0190	8418	
	0.0097	1803									
	0.0159	1795									
	0.0159	1795									
0.0036	0.0043	2912	-1096	0.0134	0.0044	6452	-4657	0.0300	0.0045	10774	-8950
	0.0053	2891			0.0049	6489			0.0052	10732	
	0.0084	2916			0.0069	6456			0.0097	10736	
	0.0088	2891			0.0088	6477			0.0111	10745	
	0.0089	2916			0.0169	6435			0.0220	10719	
	0.0168	2900			0.0173	6439			0.0221	10678	

$$\Delta H^{o}_{tr} = \Delta G^{o}_{tr} + T\Delta S^{o}_{tr}$$

where:

$$\Delta G^{o}_{tr} = -\,RT\,\ln\frac{S_{solvent}}{S_{water}}$$

$$\Delta S^{o}_{tr} = -\,\frac{\partial\Delta G^{o}_{tr}}{\partial T}$$

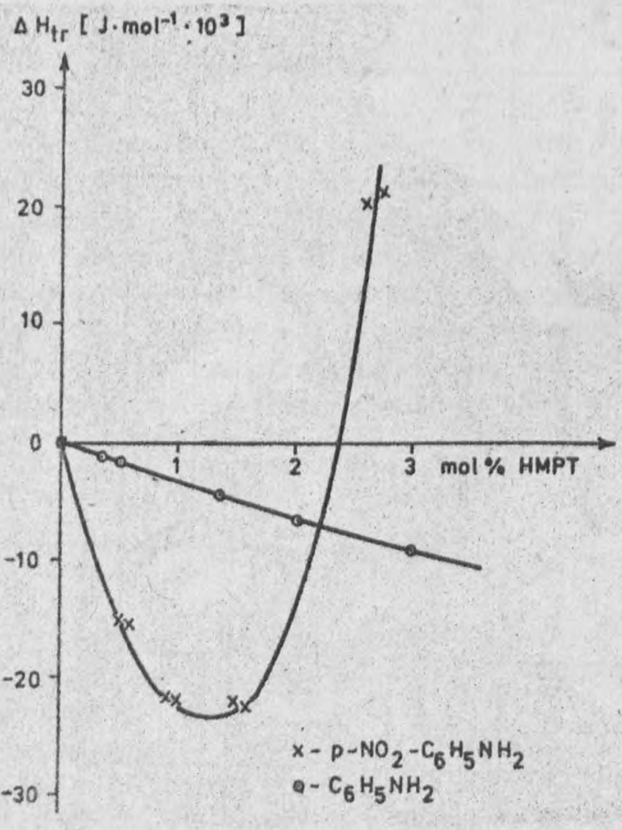

Fig. 1. Heat of transfer of $p\text{-}NO_2\text{-}C_6H_5NH_2$, $C_6H_5NH_2$ from water to HMPT-water mixtures at 298.15 K

As can be seen, the plots have different shapes. A possible reason is the presence of the $-NO_2$ group in $C_6H_5NH_2NO_2$ or a better accuracy of calorimetric measurement of ΔH^o_{tr} relative to the corresponding value determined indirectly. The difference in the shapes of the plots for aniline and p-nitroaniline aroused our interest in the course of enthalpy in the function of the composition of the mixed solvent in the case of electrolyte solutions.

In the literature available to us we have found a study of Vorobev et al. [9] concerning the measurement of KCl and KI solution enthalpy in HMPT-H_2O and the plots obtained by those authors are presented in Fig. 2.

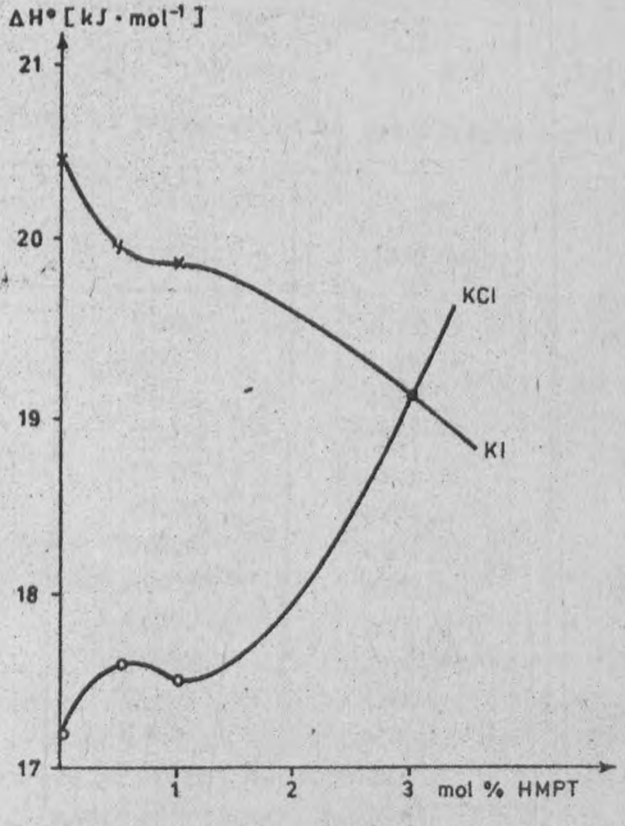

Fig. 2. Heat of solution of KCl, KI in water-HMPT mixtures at 298.15 K

It is possible that the ΔH^o data for KI and KCl in water, presented here in Fig. 2 and adopted from the paper of Vorobev et al. [9], were not determined by those authors themselves but were taken from some literature to which no reference is made. Such a conclusion is suggested by the fact that, unlike other data given in the original paper, these are not collected in the relevant table but only plotted in a figure.

In view of the different course of ΔH^o plots for KCl and KI in the function of solvent composition in comparison with the plots for aniline and p-nitroaniline, we decided to analyze Vorobev's data. To this end we determined ΔH^o for KI in water and the findings obtained are collected in Tab. 2.

Table 2

Heat of solution of KI in water at 298.15 K

x_{HMPT}	m_{KI} [mol/kg]	ΔH [J/mol]	ΔH^o [J/mol]
0.000	0.0018	20029	20040 ± 200[a] 19934 ± 200[b]
	0.0026	20056	
	0.0029	20016	
	0.0032	20010	
	0.0038	20011	
	0.0044	20001	
	0.0045	20020	
	0.0048	20028	
	0.0050	20059	
	0.0050	20048	
	0.0053	20020	
	0.0057	20026	
	0.0067	20067	
	0.0071	20074	
	0.0078	20022	
	0.0084	20059	
	0.0084	20086	

[a] Value calculated as a mean of all measurements.

[b] Value obtained by the method of Guggenheim and Prue.

The standard heat of KI solution in water was calculated by the method of Guggenheim and Prue and compared with the literature data (Tab. 3).

Table 3

Heat of solution of KI in water at 298.15 K

Authors, Year and Reference	Number of measurements	m_{KI} [mol/kg]	ΔH^o [J/mol]
Wüst, Lange 1925 [11]	24	7.95 - 0.29	20490 ± 250
Lange, Marbin 1937 [12]	1	0.11	20390 ± 250
Kapustinskii, Drakin 1952 [13]	1	0.0008	20210 ± 300
Parker's "Best" value 1965 [14]	-	-	20330 ± 130
Tsvetkov, Rabinovich 1969 [15]	1	0.111	20180 ± 250
Joly, Thourney, Pérachon 1973 [16]	-	0.0184	20580 ± 210
Efimov, Klevaichuk and al. 1979 [17]	11	0.006-0.07	20145 ± 24
Our data	17	0.0018-0.0084	20040 ± 200[a] 19934 ± 200[b]

[a] Value calculated as a mean of all measurements.

[b] Value obtained by the method of Guggenheim and Prue.

As can be seen, our result is in good agreement with most of the literature data as well as with those recommended by NBS (20.15 ± 0.2 kJ/mole) [17], while the value extracted from Vorobev's plot agrees with that obtained by Wüst and Lange [11]. Assuming that Vorobev adopted the result in question from the study of Wüst and Lange, it has to be pointed out that the latter authors calculated it from measurements made for solute concentrations of 7.95 ± 0.29 mole/kg. It thus seems that the results obtained by Efimov [17] and us are more accurate because the measurements were made for considerably more dilute solutions. To establish the degree of agreement between Vorobev's data and ours we measured the heat of KI solution in the mixed solvent containing 0.005 mol % HMPT. The value of the standard heat of solution was calculated by the method of Guggenheim and Prue. The findings callected in Tab. 4 agree - within the limit error - with those of Vorobev's.

Table 4

Heat of solution of KI in water-HMPT mixtures at 298.15 K

x_{HMPT}	m_{KI} [mol/kg]	ΔH [J/mol]	ΔH^0 [J/mol]
0.0050	0.0030	20200	20076 ± 200
	0.0035	20194	
	0.0043	20165	
	0.0043	20201	
	0.0045	20208	
	0.0056	20180	
	0.0059	20216	
	0.0060	20219	
	0.0078	20236	
	0.0089	20246	

By contrast to the method used by us Vorobev calculated the standard heat of solution using a formula - transformed by himself and his associates - describing the second approximation of Debye and Hückel [18].

In the case of the KCl plot we repeated the measurements of the heat of solution in water, and the results obtained agree - within 0.5 per cent - with those extracted from Vorobev's plot [9]. Furthermore, using the experimental data obtained by Vorobev for HMPT-water systems, we calculated the standard heat of solution by the limiting law Debye and Hückel the method of Guggenheim and Prue could not be used in view of the small number of measurements (three for each binary composition of the solvent). As can be seen in Tab. 5 and Fig. 3, the two sets of values (ours and Vorobev's) differ slightly.

Table 5

Heat of solution of KCl, KI in the water-HMPT mixtures at 298.15 K

x_{HMPT}	ΔH^o [J/mol]			
	KCl		KI	
0.000	17238[a]	17163[c]	20500[a]	19934[c]
0.005	17590 ± 30[b]	17186[d]	19980 ± 150[b]	20076[c]
0.010	17530 ± 40[b]	17336[d]	19900 ± 50[b]	19792[d]
0.030	19070 ± 40[b]	18693[d]	19090 ± 90[b]	18763[d]

[a] Data extracted from Vorobev's plot.

[b] Data cited by Vorobev.

[c] Data measured and calculated by us.

[d] Data calculated by us from Vorobev's measurements.

Table 6

Heat of transfer of the electrolytes from water to HMPT-water mixtures at 298.15 K

x_{HMPT}	ΔH^o_{tr} [J/mol]	
	KCl	KI
0.000	0	0
0.005	-23	-142
0.010	-173	+142
0.030	-1530	+1171

Taking advantage of the newly calculated data we determined the heat of electrolyte transfer from water into the mixed solvent and the results are presented in Tab. 6 and Fig. 4.

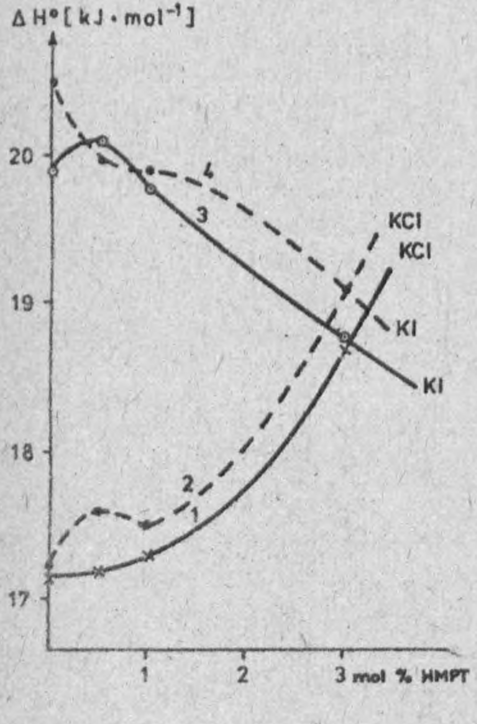

Fig. 3. Heat of solution of KCl, KI in the water-HMPT mixtures at 298.15 K. 1, 3 - data calculated by us from Vorobev's measurements; 2, 4 - data cited by Vorobev

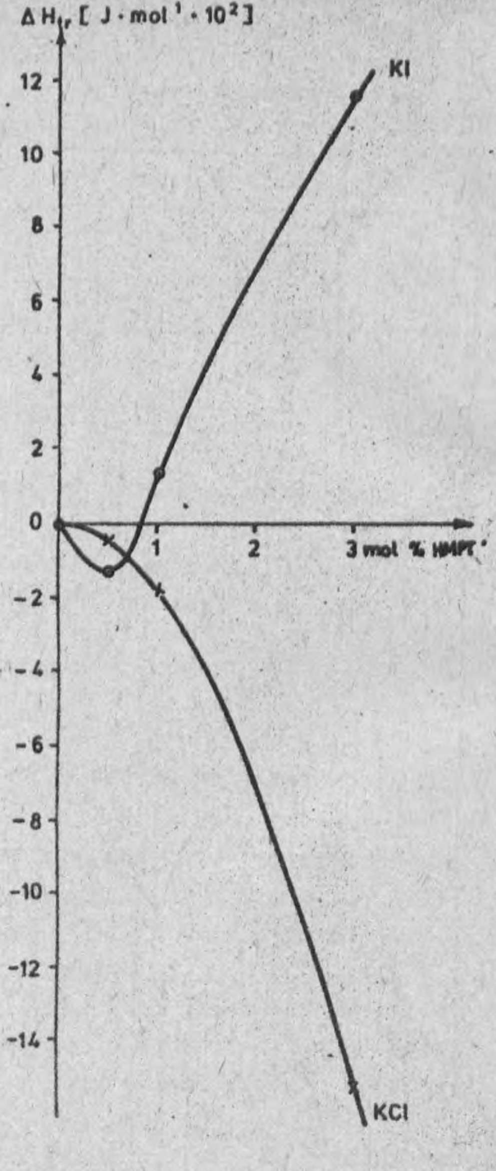

Fig. 4. Heat of transfer of the electrolytes from water to HMPT-water mixtures at 298.15 K

In every case, in the range of small HMPT content in water (up to 0.5 mol %), the enthalpy of transfer decreases. Moreover, the plots of solution enthalpies in the function of solvent composition show a distinct dependence on the kind of dissolved substance.

The present findings indicate that it is necessary to perform the relevant measurements every 0.2-0.3 mole % of the organic cosolvent. Otherwise one may overlook changes in the shape of the function under study describing the change of properties of the system. Further work on the solution enthalpy in HMPT - H_2O mixtures is in progress.

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KALORYMETRYCZNE BADANIA ROZTWORU ANILINY W MIESZANINACH HMPT-H_2O W 298.15 K

Zmierzono entalpię rozpuszczania aniliny w mieszaninach HMPT z wodą do 3% molowych HMPT w temperaturze 298.15 K. Stężenie aniliny wynosiło 0,0043-0,0221 mola/kg rozpuszczalnika mieszanego.

Dla porównania otrzymanych wyników zmierzono entalpię rozpuszczania KI w mieszaninie HMPT-H_2O. Stężenie KI wynosiło 0,0018-0,0089 mola/kg rozpuszczalnika. Na podstawie uzyskanych danych ΔH_m aniliny i KI obliczono standardową entalpię rozpuszczania (ΔH^o) i entalpię przeniesienia (ΔH^o_{tr}).

We wszystkich przypadkach w przedziale 0-0,5% molowych HMPT obserwuje się obniżenie entalpii przeniesienia.

Kształt krzywych $\Delta H^o = f$ (% molowych HMPT) zależy w sposób wyraźny od rodzaju substancji rozpuszczonej.

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КАЛОРИМЕТРИЧЕСКИЕ ИССЛЕДОВАНИЯ РАСТВОРОВ АНИЛИНА В СМЕСЯХ ГМФТ-ВОДА ПРИ 298.15 К

Измерена энтальпия растворения анилина в смесях ГМФТ-вода с содержанием ГМФТ от 0 до 3 мол. % при температуре 298.15 К. Концентрация анилина равна была 0.0045-0.0221 моль/кг растворителя. Для сравнения проведены измерения $\Delta H_м$ KI с концентрацией 0.0018-0.0034 моль/кг.

На основании полученных значений $\Delta H_м$ анилина и KI рассчитаны стандартные энтальпии растворения (ΔH^o) и энтальпии переноса ($\Delta H^o_{пер}$).

Во всех случаях в пределах 0-0.5 мол. % ГМФТ наблюдается снижение энтальпии переноса. Характер кривых $\Delta H^o = f$(мол %) с ростом содержания ГМФТ зависит от свойств растворенных соединений.