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THERMOCHEMICAL INVESTIGATION OF NaI, CsI AND LiCl SOLUTIONS IN GLYCEROL

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ABSTRACT

Measurement of the dissolution enthalpies of NaI, CsI and LiCl in the 0.008—1.5 molar concentration range has been carried out using an "isoperibol" type calorimeter in the temperature range 316.15—363.15 K. The results of the thermochemical investigations suggest the ordering effect of the mentioned salts on the structure of glycerol.

INTRODUCTION

The various applications of glycerol in pharmaceutical, cosmetic and chemical industries are well known. The wide industrial applicability of the solvent is related to its peculiar properties; some of its physico-chemical characteristics, e.g. positive value of the thermal conductivity temperature coefficient, sound propagation velocity, and negative solvation of some electrolytes, are similar to those of water. In the crystalline state, both solvents are characterized by a three-dimensional network of H-bonds [1,2]. According to some authors, glycerol, like water, partially retains the three-dimensional network of H-bonds in the liquid state [3—5], but this does not seem to have been satisfactorily established [6]. In the study reported here carlorimetric measurements were made of the solution enthalpies of NaI, CsI and LiCl in glycerol at various temperatures. These electrolytes are composed of ions of different sizes and dissolve comparatively well in glycerol. In the present study we intended to observe the effect of these salts on the properties of glycerol.

Virtually only one study [7] has so far been devoted to the enthalpy of electrolyte dissolution in glycerol (KI). However, owing to the high viscosity of the solvent at 25°C ($\eta \cong 1400$ cP), and hence the slow process of dissolution, the accuracy of measurement in that study was not very good. Therefore, we decided to conduct a thermochemical study at higher temperatures, hoping that the results obtained might be of technological interest.

EXPERIMENTAL

Reagents and apparatus

Analytical grade NaI, CsI and LiCl salts were prepared by known methods [8]. Pre-evaporated, analytical grade glycerol was dried over type 4A molecular sieves and distilled under reduced pressure. Its purity was determined by chromatography using an F-11 Perkin-Elmer chromatograph. Both in the salts and in glycerol the water content, as determined by spectrophotometry [9] (SP 700 Unicam), was below 0.02%.

Measurement of the integral heats of dissolution of NaI, CsI and LiCl in glycerol in the 0.008—1.5 mole kg^{-1} concentration range was performed in an isoperibol calorimeter [10] at temperatures between 316.15 and 363.15 K. Because of the considerable viscosity of glycerol, the stirrer of the calorimeter was additionally equipped with a spatula which thoroughly stirred the solution in the lower part of the calorimeter.

Calorimetric measurements in aqueous solutions are usually performed at 298.15 K; it therefore seemed necessary to select a measurement temperature of glycerol solutions corresponding to 298.15 K.

As the effects of temperature changes on the properties of individual solvents are different, it seemed that the most suitable criterion for selecting temperatures corresponding to 298.15 K would be a constant value of the T/T_m ratio, where T_m is the melting point and T is the experimental temperature [11] by calculating this ratio for one solvent, it is possible to determine the corresponding temperature for some other solvent. For water at 298.15 K the T/T_m ratio is 1.09. Multiplying the melting point for glycerol (290 K) by the 1.09 factor gives ca. 316 K, which corresponds to 298.15 K, i.e. the temperature at which the majority of investigations are performed.

RESULTS AND DISCUSSION

The measurements of the integral heats of solution of NaI and CsI in glycerol were performed at 316.15, 333.15 and 353.15 K, while for LiCl they were performed at higher temperatures, viz. 343.15, 353.15 and 363.15 K due to experimental difficulties the low specific weight of LiCl caused it to collect on the surface.

Tables 1—3 give the values of the solution enthalpies of the salts in glycerol. Figures 1—3 represent the course of the $\Delta H_m = f(m)$ function for the investigated solutions.

As can be seen, the solution process of NaI and LiCl is exothermic and that of CsI is endothermic, similar to the case of aqueous solutions of these electrolytes. The standard enthalpies of dissolution, ΔH^0, were determined by the Guggenheim and Prue procedure [12], and are listed in Table 4.

On the basis of the ΔH^0 values obtained, it was possible to determine the relative partial molal enthalpy of glycerol, $\bar{L}_1$, and then the $\bar{L}_1/T$ quotient. As is well known, the structural changes of the solvent are best reflected in the entropy, $\Delta\bar{S}_1^E$ [13,14]. In the present study, we were unable to experi-

TABLE 1

Enthalpy of solution, ΔH_m, of NaI in glycerol

316.15 K		333.15 K		353.15 K	
m (mole kg^{-1})	$-\Delta H_m$ (kcal $mole^{-1}$)	m (mole kg^{-1})	$-\Delta H_m$ (kcal $mole^{-1}$)	m (mole kg^{-1})	$-\Delta H_m$ (kcal $mole^{-1}$)
0.01051	6.05	0.00861	6.24	0.01312	6.52
0.02543	6.00	0.02533	6.11	0.03792	6.35
0 05542	5.92	0 06213	6.09	0.04230	6.29
0 09240	5.85	0.07020	6.03	0.05787	6.22
0.12054	5.78	0 10372	5.99	0.11255	6.15
0.13030	5.72	0.15845	5.85	0 11370	6.03
0.18222	5.69	0.22316	5.78	0.17753	6.01
0.21255	5 62	0 26091	5.72	0 23781	5.95
0 28607	5.56	0.32882	5.65	0.28820	5.87
0.38891	5.49	0 36494	5.60	0.34654	5.79
0 48332	5.39	0.47560	5.52	0.40573	5 72
0.57862	5.35	0.59193	5.44	0 52097	5 60
0.66634	5.27	0.70873	5.34	0.66538	5.49
0.75708	5.21	0.84012	5 30	0.81719	5 41
		0.96124	5.23	0.96891	5 31
		1.08575	5.17	1.17410	5 23
				1.36065	5.17

TABLE 2

Enthalpy of solution, ΔH_m, of CsI in glycerol

316 15 K		333 15 K		353.15 K	
m (mole kg^{-1})	ΔH_m (kcal $mole^{-1}$)	m (mole kg^{-1})	ΔH_m (kcal $mole^{-1}$)	m (mole kg^{-1})	ΔH_m (kcal $mole^{-1}$)
0 00951	3 24	0.01031	3.04	0.00894	2.83
0 01862	3.27	0.02612	3.09	0.01933	2 88
0 02960	3.31	0 03544	3 13	0.03092	2 93
0.06150	3.35	0.05714	3.18	0 05050	3.00
0.09223	3 40	0.08525	3.21	0.07121	3.04
0 12645	3 44	0.11918	3.27	0 07520	3.09
0.15674	3.50	0.15417	3.31	0.14944	3.20
0.20053	3.52	0.19030	3.35	0 20075	3 26
0.27222	3.60	0.23604	3.42	0 24460	3.29
0 34121	3.65	0.28183	3.46	0 31523	3.36
		0.32952	3.48	0.35803	3.38
		0.37880	3.52	0.41374	3.42
		0.45731	3.54	0.47785	3.48
		0 53754	3.65	0.53628	3.50
				0.59467	3.55

TABLE 3

Enthalpy of solution, ΔH_m, of LiCl in glycerol

343.15 K		353.15 K		363.15 K	
m (mole kg^{-1})	$-\Delta H_m$ (kcal $mole^{-1}$)	m (mole kg^{-1})	$-\Delta H_m$ (kcal $mole^{-1}$)	m (mole kg^{-1})	$-\Delta H_m$ (kcal $mole^{-1}$)
0.00984	8.12	0.01054	8.62	0.01224	9.21
0.02232	8.08	0.02370	8.55	0.02283	9.12
0 03495	8.04	0 03577	8.50	0.04062	9.02
0 08048	7.91	0.08120	8 38	0.07520	8 86
0.13617	7.87	0.12874	8.27	0.10410	8.68
0 18820	7.77	0.17713	8.17	0.13785	8.59
0.24814	7.70	0.24002	8.07	0 16956	8.50
0.32001	7.64	0.28241	8.01	0.16956	8.50
0 35003	7.61	0.33909	7 93	0.24490	8.38
		0.40998	7.84	0 32167	8.21
		0.44937	7.79	0.38813	8.12
				0.46274	8 01
				0.50232	7 95

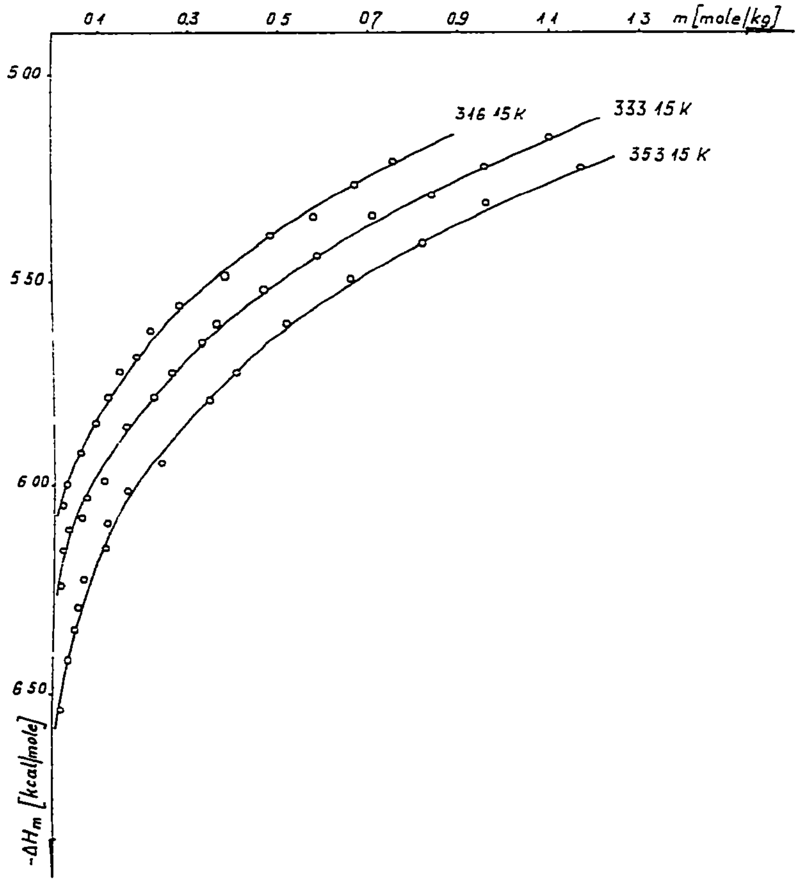

Fig. 1. Enthalpy of solution of NaI in glycerol.

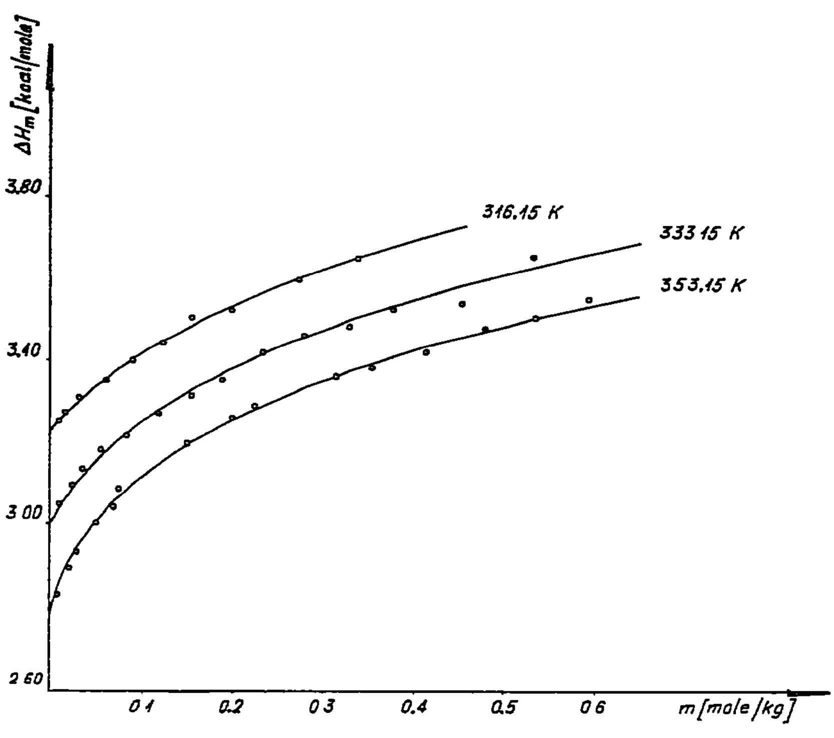

Fig. 2. Enthalpy of solution of CsI in glycerol.

mentally determine that function as it is difficult to determine glycerol activity using conventional methods. But, as has been demonstrated by Mishchenko and Sokolov [15], functions $\Delta\bar{S}_1^E = f(m, T)$ and $\bar{L}_1/T = f(m, T)$ in aqueous solutions change in the same way. It thus seems that changes in $\bar{L}_1/T$ can provide some information about the effect of the salts under investigation on the structure of glycerol.

As can be seen from Figs. 4—6 the function $\bar{L}_1/T$ has negative values in the case of all solutions under study. This indicates that these salts probably have an ordering effect on the structure of glycerol, because in the case of aqueous solutions the salts which have an ordering effect on the structure of water also have negative $\Delta\bar{S}_1^E$ or $\bar{L}_1/T$ values.

It follows from the results presented above that the temperature coefficient, ΔH^0, has a negative value over the entire range of concentrations and temperatures, similar to the case of all aqueous solutions of alkali halides that have so far been investigated [14]. In non-aqueous solutions, the above coefficient may have either positive or negative values, depending on the kind of electrolyte and temperature [16]. According to some authors [16], the structure of the electrolyte solution can be better assessed by analyzing the function $\bar{c}_{p2}^0$, but the procedure requires other precise measurements.

It seems that neither the sign of the temperature coefficient, ΔH^0, nor the $\bar{c}_{p2}^0$ function unequivocally demonstrate the peculiar properties of water. Our earlier thermochemical and viscosimetric study [17] of the acetamide solutions of electrolytes showed acetamide to be similar to water. To some extent the same applies to glycerol, which we studied thermochemically as a

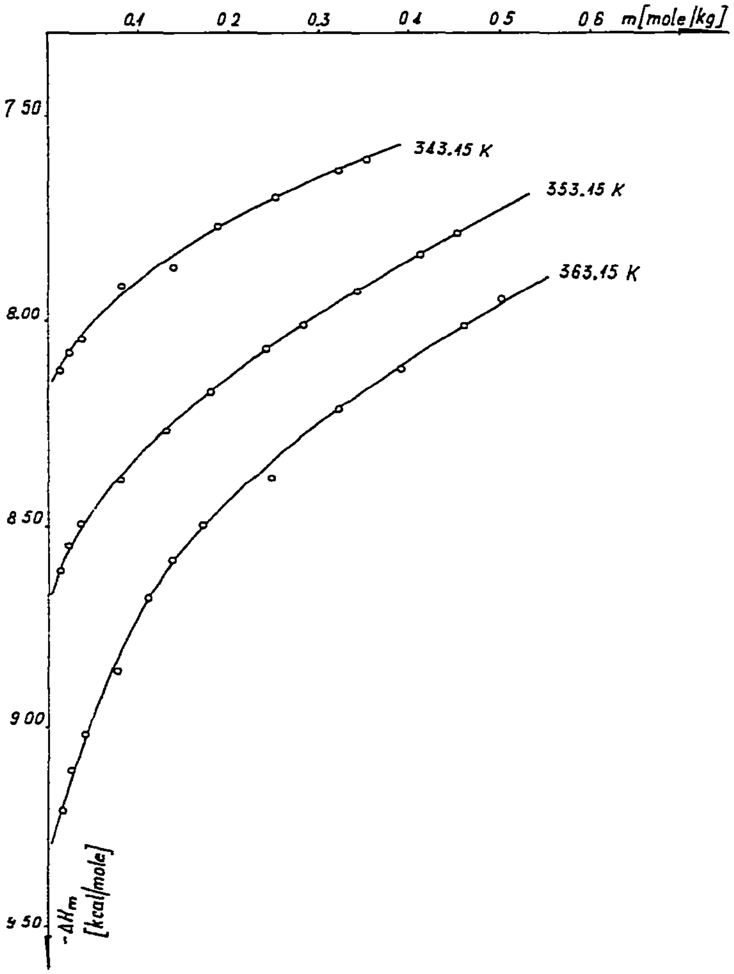

Fig. 3. Enthalpy of solution of LiCl in glycerol.

solvent of electrolytes. In view of the above, it seems that the distinction between water and non-aqueous (organic) solvents is not entirely justified, especially if based on some investigations of electrolyte solutions in these

TABLE 4

Standard enthalpy of solution (kcal mole^{-1}) of salts at various temperatures

T (K)	316.15	333.15	353.15
ΔH^0			
NaI	−6.13	−6.45	−6.84
CsI	3.02	2.80	2.53
T (K)	343.15	353.15	363.15
ΔH^0			
LiCl	−8.35	−8.95	−9.60

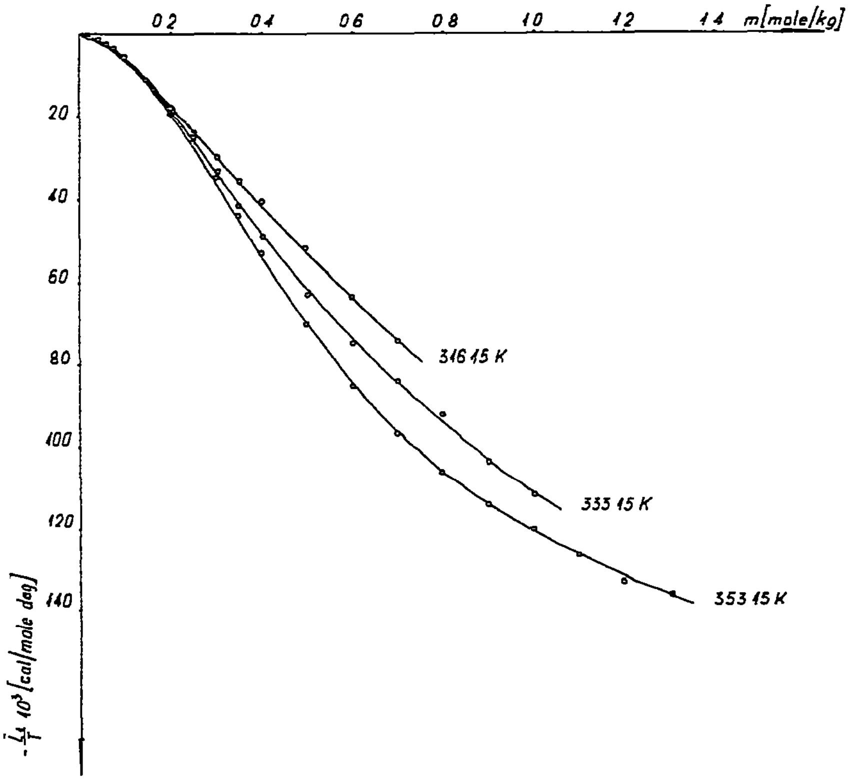

Fig. 4. The quotient of relative partial molal solvent enthalpy and temperature in glycerol solutions of NaI.

solvents. According to Evans and Matesich [18], electrolytes behave similarly in water and in all solvents which contain ordered structures related to the presence of H-bonds.

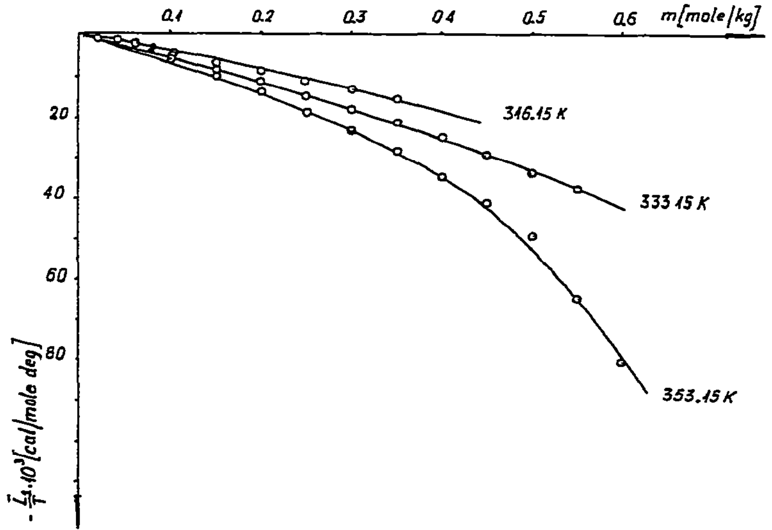

Fig. 5. The quotient of relative partial molal solvent enthalpy and temperature in glycerol solutions of CsI.

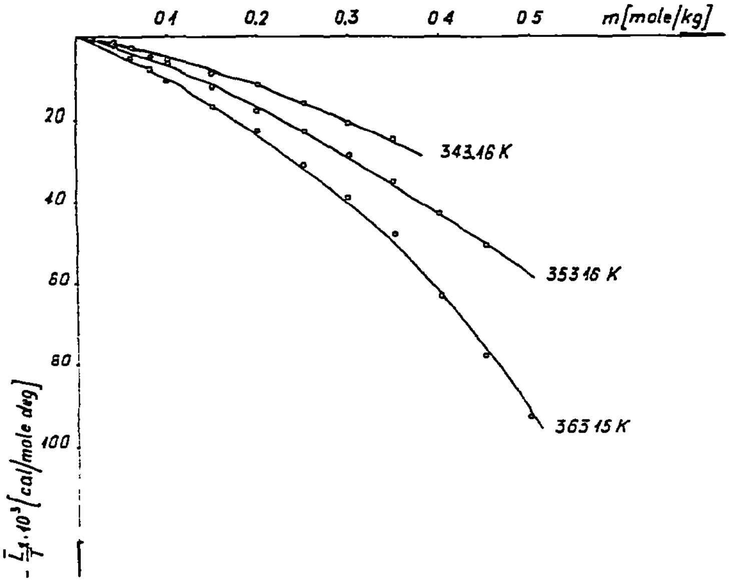

Fig. 6. The quotient of relative partial molal solvent enthalpy and temperature in glycerol solutions of LiCl.

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