A C T A   U N I V E R S I T A T I S   L O D Z I E N S I S
FOLIA CHIMICA 2, 1983

Stefania Taniewska-Osińska, Jadwiga Woźnicka

RELATIVE PARTIAL MOLAL ENTHALPY OF GLYCEROL ($\bar{L}_1$) AND OF ELECTROLYTES ($\bar{L}_2$) AT SEVERAL TEMPERATURES

The velues of the relative partial molal enthalpy of glycerol ($\bar{L}_1$) and of NaI, CsI, LiCl ($\bar{L}_2$) within the temperature range 43--90°C were obtained. The course of the function of the $\bar{L}_1$, $\bar{L}_2$ and $\bar{L}_1/T$ vs. salt concentration and temperature has been discussed.

As it was mentioned earlier [1] glycerol shows some similarities of its physico-chemical properties to water. In one of our papers [1] we presented the NaI, CsI and LiCl enthalpy of solution in glycerol within the temperature range 43-90°C. The intention of this work was to find the influence of the mentioned above electrolytes on glycerol properties as well as to observe some similarities between water and glycerol used as electrolyte solvents.

Our experimental results may be described by means of the following 3rd order polynomial.

$$\Delta H_m = A_o + A_1 m + A_2 m^2 + A_3 m^3 \qquad (1)$$

where:

ΔH_m - integral enthalpy of solution;

m - electrolyte concentration (in mol./kg of solvent);

A_o, A_1, A_2, A_3 - polynomial coefficients.

Using the above polynomial we calculated: the solution heat in infinitely diluted solution (ΔH^o), integral dilution heat ΔH_m^o, the temperature coefficients of solution enthalpy $d\Delta H_m/dT$,

Table 1

Relative partial molal enthalpy of glycerol - $\bar{L}_1$ and NaI - $\bar{L}_2$ at investigated temperatures

m [mol./kg]	43°C	55°C	60°C	70°C	80°C
		$\bar{L}_1$ [cal/mol.]			
0.00	0.0	0.0	0.0	0.0	0.0
0.02	-0.1	-0.1	-0.1	-0.1	-0.1
0.06	-0.7	-0.7	-0.7	-0.7	-0.7
0.10	-1.9	-1.8	-1.7	-1.7	-1.8
0.20	-5.7	-5.9	-5.9	-6.0	-6.4
0.30	-9.5	-10.9	-11.0	-11.7	-12.4
0.40	-12.8	-15.8	-16.4	-17.7	-18.8
0.50	-16.4	-20.1	-21.2	-23.4	-24.9
0.60	-20.3	-23.6	-25.1	-28.3	-30.2
0.80	-25.4	-29.9	-30.8	-35.5	-37.7
0.90		-31.9	-34.7	-38.1	-40.1
1.00		-33.7	-37.3	-40.8	-42.4
1.10			-38.3	-42.2	-45.2
1.20				-43.1	-46.2
1.30					-47.0
		$\bar{L}_2$ [cal/mol.]			
0.00	0.0	0.0	0.0	0.0	0.0
0.02	1.3	0.8	0.6	0.6	0.6
0.06	10.8	6.6	5.6	5.1	5.2
0.10	28.6	17.7	15.2	13.7	14.2
0.20	100.7	72.3	57.0	51.8	53.6
0.30	195.3	145.5	125.2	119.6	113.7
0.40	293.6	229.6	218.0	198.3	189.7
0.50	404.2	340.0	312.5	295.3	277.0
0.60	523.4	448.6	411.4	393.9	370.9
0.80	795.2	658.7	604.1	579.1	359.8
0.90		765.3	696.1	676.3	645.4
1.00		862.3	797.4	770.4	732.2
1.10			891.9	866.5	825.1
1.20				953.2	918.2
1.30					980.5

Table 2

Relative partial molal enthalpy of glycerol - $\bar{L}_1$ and CsI - $\bar{L}_2$ at investigated temperatures

m [mol./kg]	43°C	55°C	60°C	70°C	80°C
			$\bar{L}_1$ [cal/mol.]		
0.00	0.0	0.0	0.0	0.0	0.0
0.02	-0.1	-0.1	-0.1	-0.1	-0.1
0.06	-0.6	-0.6	-0.7	-0.8	-0.9
0.10	-1.5	-1.6	-1.7	-1.8	-2.0
0.20	-2.4	-2.9	-3.4	-4.3	-4.8
0.30	-3.9	-4.8	-5.6	-6.7	-8.2
0.40		-7.1	-7.9	-8.9	-12.1
0.50			-11.0	-12.8	-17.3
0.60				-18.2	-40.5
			$\bar{L}_2$ [cal/mol.]		
0.00	0.0	0.0	0.0	0.0	0.0
0.02	82.2	93.1	101.9	113.0	125.2
0.06	256.4	253.4	274.3	303.1	331.5
0.10	336.9	382.1	409.4	450.5	486.4
0.20	533.9	591.7	618.9	673.1	703.0
0.30	649.2	689.0	712.2	766.2	838.4
0.40		734.2	772.9	853.1	953.9
0.50			834.5	907.0	1051.3
0.60				953.4	1505.6

Table 3

Relative partial molal enthalpy of glycerol - $\bar{L}_1$ and LiCl - $\bar{L}_2$ at investigated temperatures

m [mol./kg]	70^oC	75^oC	80^oC	85^oC	90^oC
			$\bar{L}_1$ [cal/mol.]		
0.00	0.0	0.0	0.0	0.0	0.0
0.02	-0.1	-0.1	-0.1	-0.1	-0.2
0.06	-0.9	-1.0	-1.0	-1.1	-1.8
0.10	-1.9	-2.8	-2.8	-2.9	-4.0
0.20	-4.1	-4.8	-6.4	-7.5	-8.4
0.30	-7.2	-9.0	-10.3	-11.8	-14.3
0.40		-13.1	-15.3	-19.0	-23.1
0.50				-30.9	-56.0
			$\bar{L}_2$ [cal/mol.]		
0.00	0.0	0.0	0.0	0.0	0.0
0.02	4.2	4.7	5.3	5.8	6.2
0.06	34.0	39.2	42.3	48.7	51.3
0.10	83.1	97.2	109.6	119.8	130.4
0.20	219.3	293.5	268.4	330.8	400.6
0.30	289.0	350.4	400.7	510.2	629.3
0.40		438.5	541.3	646.2	758.2
0.50				741.3	837.3

relative partial molal enthalpy of solvent $\bar{L}_1$ and of electrolytes $\bar{L}_2$ and the quotient of $\bar{L}_1/T$.

We have discussed here the following functions: $\bar{L}_1 = f(m, T)$, $\bar{L}_2 = f(m, T)$ and $\bar{L}_1/T = f(m, T)$.

It is known [2] that the relative partial molal enthalpy of solvent and of electrolyte can be calculated from relations:

$$\bar{L}_1 = \frac{m\sqrt{m}}{2} \cdot \frac{M}{1000} \cdot \frac{d\,(\Delta H_m^o)}{d\sqrt{m}} \qquad (2)$$

$$\bar{L}_2 = -\Delta H_m^o - \frac{\sqrt{m}}{2} \frac{d(\Delta H_m^o)}{d\sqrt{m}} \quad (3)$$

Our $\bar{L}_1$ and $\bar{L}_2$ values for NaI, CsI and LiCl glycerol solutions within the investigated temperature range are presented in tab. 1-3.

It is seen from tables that the values of $\bar{L}_1$ function are negative within the investigated temperature and concentration ranges. Negative $\bar{L}_1$ values show that the vaporization heat of the solvent from solution is higher in comparison to the vaporization enthalpy of pure solvent. It may be suggested that the investigated salts cause the solvent structure ordering. Function $\bar{L}_2$ shows the positive values and increases with the concentration growth. The shapes of $\bar{L}_1 = f(m, T)$ and $\bar{L}_2 = f(m, T)$ curves are characteristic for the I-type isoterms of aqueous electrolyte solutions [3]. This group of salts exerts the water structure ordering effect.

It is known that the solution structure changes are shown in the best way by means of entropy changes [2, 4]. To determine the excess of relative partial molal entropy of solvent $\Delta\bar{S}_1^E$ the solvent activity a_1 must be known.

$$\Delta\bar{S}_1^E = \frac{\bar{L}_1 - RT\ln\frac{a_1}{x_1}}{T} \quad (4)$$

The glycerol activities in NaI, CsI and LiCl solutions are unknown within the used temperature range which is probably due to the glycerol physico-chemical properties making appropriate experiments difficult to carry out. We used $\bar{L}_1$ values for the determination of $\bar{L}_1/T$ quotient. The function $\bar{L}_1/T = f(m, T)$ shows the same character of changes as a $\Delta\bar{S}_1^E = f(m, T)$ function in the aqueous and organic solutions [5].

Our $\bar{L}_1/T$ values for glycerol solutions are presented in the tab. 4-6. As it is seen $\bar{L}_1/T$ shows negative values for NaI, CsI and LiCl glycerol solutions. Absolute $\bar{L}_1/T$ values increase with concentration and temperature growth. This fact suggests also the ordering effect of investigated salts on the structure of glycerol.

Table 4

The ratio $\bar{L}_1/T \cdot 10^3$ [cal/mol. deg] of glycerol solutions of NaI at investigated temperatures

m [mol./kg]	43°C	55°C	60°C	70°C	80°C
0.00	0.0	0.0	0.0	0.0	0.0
0.02	-0.2	-0.2	-0.2	-0.2	-0.2
0.06	-2.4	-2.1	-2.0	-1.9	-2.0
0.10	-5.9	-5.4	-5.2	-5.1	-5.2
0.20	-17.9	-17.9	-17.5	-17.6	-18.1
0.30	-30.2	-33.2	-33.2	-34.0	-35.1
0.40	-40.6	-48.3	-49.2	-51.6	-53.3
0.50	-51.9	-61.2	-63.6	-68.2	-70.6
0.60	-64.3	-71.9	-75.4	-82.6	-85.6
0.80	-80.3	-91.1	-92.5	-103.4	-106.7
0.90		-97.1	-104.2	-111.0	-113.7
1.00		-102.8	-112.1	-118.9	-120.1
1.10			-115.1	-123.1	-128.1
1.20				-125.7	-130.8
1.30					-133.2

Table 5

The ratio $\bar{L}_1/T \cdot 10^3$ [cal/mol. deg] of glycerol solutions of CsI at investigated temperatures

m [mol./kg]	43°C	55°C	60°C	70°C	80°C
0.00	0.0	0.0	0.0	0.0	0.0
0.02	-0.3	-0.3	-0.3	-0.3	-0.3
0.06	-1.9	-2.0	-2.1	-2.3	-2.4
0.10	-3.8	-4.9	-5.1	-5.4	-5.6
0.20	-7.8	-9.1	-10.4	-12.5	-13.7
0.30	-12.6	-14.8	-16.9	-20.1	-23.3
0.40		-21.8	-24.0	-25.9	-34.4
0.50			-33.1	-37.3	-48.9
0.60				-53.2	-114.8

Table 6

The ratio $\bar{L}_1/T \cdot 10^3$ [cal/mol. deg] of glycerol solution of LiCl at investigated temperatures

m [mol./kg]	70°C	75°C	80°C	85°C	90°C
0.00	0.0	0.0	0.0	0.0	0.0
0.02	-0.4	-0.3	-0.3	-0.4	-0.7
0.06	-2.6	-3.1	-2.7	-3.2	-4.9
0.10	-5.6	-8.1	-6.7	-8.0	-11.2
0.20	-12.1	-13.8	-18.3	-21.0	-23.1
0.30	-21.1	-26.1	-29.1	-33.0	-39.4
0.40		-37.8	-43.5	-53.1	-63.5
0.50				-86.5	-154.3

REFERENCES

[1] Taniewska-Osińska S., Woźnicka J., Termodinamika i stroyeniye rastvorov, "Miezvuzovskii Sbornik", 3, 133 (1976).

[2] Mishchenko K. P., Poltoratskii G. M., Voprosy termodynamiki i stroyeniya vodnykh i nevodnykh rastvorov elektrolitov, Leningrad (1968).

[3] Mishchenko K. P., Pronina M. Z., Zhur. Obsh. Khim., 6, 85 (1936).

[4] Frank H. S., Robinson A. L., J. Chem. Phys., 8, 933 (1940).

[5] Mishchenko K. P., Sokolov V. V., Zhur. Strukt. Khim., 4, 184 (1963).

Institute of Chemistry
University of Łódź

Stefania Taniewska-Osińska, Jadwiga Woźnicka

WZGLĘDNA CZĄSTKOWA MOLOWA ENTALPIA GLICERYNY ($\bar{L}_1$) I ELEKTROLITÓW ($\bar{L}_2$) W KILKU TEMPERATURACH

W wyniku pomiarów kalorymetrycznych uzyskano wartości względnej cząstkowej molowej entalpii gliceryny $\bar{L}_1$ oraz elektrolitów: NaI, CsI i LiCl - $\bar{L}_2$ w zakresie temperatur 43-90°C. Przedyskutowano następnie charakter zmian następujących funkcji: $\bar{L}_1 = f(m, T)$, $\bar{L}_2 = f(m, T)$ oraz ilorazu $\bar{L}_1/T = f(m, T) \approx \Delta\bar{S}_1^E = f(m, T)$. Znak wspomnianych funkcji oraz kierunek ich zmian wraz ze zmianą stężenia i temperatury sugerują porządkujący wpływ badanych soli na strukturę gliceryny.

Стефания Таневска-Осинска, Ядвига Возницка

ОТНОСИТЕЛЬНАЯ ПАРЦИАЛЬНАЯ МОЛЯРНАЯ ЭНТАЛЬПИЯ ГЛИЦЕРИНА ($\bar{L}_1$) И ЭЛЕКТРОЛИТОВ ($\bar{L}_2$) В НЕСКОЛЬКИХ ТЕМПЕРАТУРАХ

Калориметрическим методом получено значение относительной парциальной молярной энтальпии $\bar{L}_1$ глицерина и $\bar{L}_2$ электролитов: NaI, CsI и LiCl в диапазоне температур 43-90°C. Проанализирован характер хода следующих функций: $\bar{L}_1 = f(m, T)$, $\bar{L}_2 = f(m, T)$, $\bar{L}_1/T = f(m, T) \approx \Delta\bar{S}_1^E = f(m, T)$. Значения этих функций и характер хода указывают на упорядочивающее влияние изученных солей на структуру глицерина.