

## **CHAPTER XII**

### **Conductometric Study of Some Metal Halides in Glycerol + Water Mixtures**

#### **12.1. Introduction**

Transport properties are very useful for the study of ionic solvation. These properties can give information on the effective size of a moving particle in solution. These properties are sensitive to strong ion-solvent interactions, which increase the effective size of the ions and also any modification in the structure of the solvent.<sup>1-2</sup> Shehata *et al.*<sup>3-4</sup> studied the electrical conductivities of  $\text{Ba}(\text{NO}_2)_2$  and  $\text{Sr}(\text{NO}_3)_2$  in glycerol +  $\text{H}_2\text{O}$  mixtures to determine the nature of ionic associations and mobility of ions in this mixed solvent system. In the present study, an attempt has been made to ascertain the nature of ion-solvent interactions of potassium halides (chloride, bromide and iodide) in glycerol +  $\text{H}_2\text{O}$  mixtures using the conductometric technique. Thermodynamic parameters are also evaluated and discussed.

#### **12.2. Experimental Section**

##### **12.2.1 Materials**

Potassium metal salts (KCl, KBr and KI) were of puris or purum grade (Fluka), quoted as 99.5% pure and were purified as described earlier.<sup>5, 6</sup> Water was double distilled and then passed through a column containing mixed resin (anion-cation exchange). Glycerol (G.R.E. Merck, India, >99.5%) was purified as described earlier.<sup>7</sup>

##### **12.2.2 Apparatus and procedures**

The densities ( $\rho$ ) were measured with an Ostwald-Sprengel type pycnometer having a bulb volume of  $25 \text{ cm}^3$  and an internal diameter of the capillary of about 0.1 cm. The pycnometer was calibrated at 298.15, 308.15, and 318.15 K using doubly-distilled water and benzene. The pycnometer with the test solution was equilibrated in a water bath maintained at  $\pm 0.01^\circ\text{C}$  of the desired temperature by means of a mercury-in-glass thermo

regulator and the temperature was determined with a calibrated thermometer and a Muller bridge. The pycnometer was then removed from the thermostatic bath, properly dried and weighed. The evaporation losses remained insignificant during the time of actual measurements. The density values were reproducible to  $\pm 3 \times 10^{-3}$  g.cm<sup>-3</sup>. Details have been described earlier.<sup>9-11</sup> A stock solution for each salt was prepared by mass, and the working solutions were obtained by mass dilution. The conversion of molality to molarity was done using the density values.<sup>8</sup>

The viscosities were measured by means of a suspended level Ubbelohde viscometer at the desired temperature (uncertainty of  $\pm 0.01^\circ\text{C}$ ). The precision of the viscosity measurement was  $\pm 0.005$  mPa.s. Details have been described earlier.<sup>12-13</sup>

Conductance measurements were carried out with a Systonic-306 conductivity bridge using a dip-type cell (cell constant = 0.1 cm<sup>-1</sup>) with an uncertainty of  $\pm 0.01\%$ . The cell was calibrated by the method of Lind and co-workers<sup>14</sup> using aqueous potassium chloride solutions. Measurements were made as described earlier.<sup>15</sup> Several independent solutions were prepared and conductance measurements were performed with each of these to ensure the reproducibility of the results. Corrections were made for the specific conductance of the solvent.

The conductance values of 10 mass% glycerol + H<sub>2</sub>O mixture were  $5.08 \times 10^{-5}$ ,  $6.63 \times 10^{-5}$ , and  $8.18 \times 10^{-5}$  S.cm<sup>-1</sup> at 298.15, 308.15, and 318.15 K respectively. The concentrations of measured solutions were in the range of  $6.86 \times 10^{-3}$  to  $8.68 \times 10^{-2}$  mol.dm<sup>-3</sup>.

### 12.3. Results and discussion

Molar conductances ( $\Lambda$ ), densities ( $\rho$ ) and molar concentrations ( $c$ ) are given in Table 1 in different solvent mixtures at 298.15, 308.15, and 318.15 K. The solvent properties of glycerol + H<sub>2</sub>O mixtures are given in Table 2. Dielectric constants of the solvent mixture were obtained by extrapolation of  $\epsilon$  (dielectric constant) versus  $W$  (the mass of glycerol in the aqueous mixtures) plots; the original values were taken from the work of Akerlof.<sup>16</sup>

The conductance data have been analyzed by the Fuoss conductance-concentration equation.<sup>17-18</sup> For a given set of conductivity values

$(c_j, A_j, j = 1, \dots, n)$ , three adjustable parameters, the limiting molar conductivity ( $\Lambda^0$ ), the association constant ( $K_A$ ) and the distance of closest approach of ions ( $R$ ) are derived from the following set of equations:

$$\Lambda = p[\Lambda_0(1 + R_x) + E_L] \quad (1)$$

$$p = 1 - \alpha(1 - \gamma) \quad (2)$$

$$\gamma = 1 - K_A c \gamma^2 f^2 \quad (3)$$

$$-\ln f = \beta \kappa / 2(1 + K_R) \quad (4)$$

$$\beta = e^2 / \epsilon K_B T \quad (5)$$

$$K_A = K_R / (1 - \alpha) = K_R(1 + K_S) \quad (6)$$

where  $R_x$  is the relaxation field effect,  $E_L$  is the electrophoretic counter current constant,  $\kappa^{-1}$  is the radius of the ionic atmosphere,  $\epsilon$  is the relative permittivity of the solvent,  $e$  is the electric charge,  $K_B$  is the Boltzmann constant,  $\gamma$  is the fraction of solute present as unpaired ion,  $c$  is the molarity of the solution,  $f$  is the activity coefficient,  $T$  is the temperature in absolute scale,  $\beta$  is twice the Bjerrum distance,  $K_R$  describes the formation and separation of solvent separated pairs by diffusion in and out of sphere of diameter  $R$  around cations and  $K_S$  is a constant describing the short-range process by which contact pairs forms and dissociates.

We input for the program the number of data,  $n$ ; followed by dielectric constant of the solvent mixture,  $\epsilon$ ; initial  $\Lambda_0$  values,  $T$ ,  $\rho$ , molecular weight of the solvents along with  $c_j$ ,  $A_j$  values where  $j=1, 2, \dots, n$  and an instruction to cover pre-selected range of  $R$ -values.

In practice calculations, were performed by finding the values of  $\Lambda_0$  and  $\sigma$ , which minimized the standard deviation ( $\sigma$ ),

$$\sigma^2 = \sum_{j=1}^n \frac{[\Lambda_j(\text{calc}) - \Lambda_j(\text{obs})]^2}{(n-2)} \quad (7)$$

for a sequence of  $R$ -values and then plotting  $\sigma$  against  $R$ ; The best-fit  $R$  corresponds to the minimum of the  $\sigma$  versus  $R$  curve. First, approximate run over a fairly wide range of  $R$ -values were made to locate the minimum,

and then a fine scan around the minimum was made. Thus, the corresponding  $\Lambda_0$  and  $K_A$  values were noted.

Here  $R$  is the association distance, i.e. the maximum centre-to-centre distance between the ions in the solvent separated ion-pairs. There is no precise method for determining the  $R$ -value but in order to treat the data in our system,  $R$ -value is assumed to be,  $R = a + d$ ; where  $a$  is the sum of the crystallographic radii of ions, which varies from 2 to 7 Å and  $d$  is the average distance corresponding to the side of a cell occupied by a solvent molecule. The distance  $d$ (Å) is given by,

$$d = 1.183(M/\rho_0)^{1/3} \quad (8)$$

where  $M$  is the molecular weight and  $\rho_0$  is the density of the solvent. For mixed solvents,  $M$  is replaced by the mole fraction average molecular weight ( $M_{AV}$ ), which is given by,

$$M_{AV} = M_1 M_2 / [W_1 M_2 + W_2 M_1] \quad (9)$$

where  $W_1$  is the weight fraction of the first component of molecular weight  $M_1$  and  $W_2$  is the weight fraction of the second component of molecular weight  $M_2$ . Though, this is an over simplification which ignores possible selective solvation, it at least provides a self-consistent way to obtain an acceptable value for the parameters when a broad range of  $R$ -values fit the data. The values of  $\Lambda^0$ ,  $K_A$  and  $R$  obtained by this procedure are reported in Table 3. Inspection of the data of Table 3 shows that the values of  $\Lambda^0$  of all salts decrease as the concentration of glycerol in the aqueous mixtures increases. But as the temperature increases,  $\Lambda^0$  values increase for all glycerol + H<sub>2</sub>O mixtures. The trends in  $\Lambda^0$  can be discussed through another characteristic function called the Walden product,  $\Lambda^0 \eta^0$ . Although  $\Lambda^0$  decreases as the concentration of glycerol increases;  $\Lambda^0 \eta^0$  (Table 4) increases due to the increase of the viscosity ( $\eta$ ). The  $\Lambda^0 \eta^0$  decreases with an increase in temperature at 298.15, 308.15 and 318.15 K for all glycerol + H<sub>2</sub>O mixtures. The decrease in  $\Lambda^0 \eta^0$  is small. The decrease in  $\Lambda^0 \eta^0$  with temperature, which is common in aqueous solutions,<sup>19</sup> can probably be

interpreted as a thermal expansion of the solvent sheath (which envelops an ion and moves by ion-solvent interactions, *i.e.*, the expansion of a solvated ion, because of the activation of solvent molecules forming the sheath.

From Table 3, we see that  $\Lambda^0$  of potassium salts of common cations follow the sequence:  $\text{Cl}^- < \text{Br}^- < \text{I}^-$ . Furthermore,  $\Lambda^0$  of the studied electrolyte is enhanced in the following order:  $\text{KI} > \text{KBr} > \text{KCl}$ . The sizes of these anions as they exist in solution follow the order:  $\text{Cl}^- > \text{Br}^- > \text{I}^-$ . This shows that potassium halides with  $\text{Cl}^-$  is most solvated and those with having  $\text{I}^-$  are the least solvated one in all concentrations of glycerol +  $\text{H}_2\text{O}$  mixtures. A Similar result<sup>6</sup> was obtained in conductance studies of alkali metal chlorides and bromides in THF + water mixtures at 298.15 K.

There are marked characteristic behaviors in the  $K_A$  values.  $K_A$  generally decreases as the temperature is increased; the thermal motion probably destroys the solvent structure. However,  $K_A$  for all salts increases as the concentration of glycerol increases in the mixture.

Since the conductance of an ion depends on rate of movement, it seems reasonable to treat that the conductance in a manner analogous to that employed for other processes taking place at a definite rate, which increases with temperature.<sup>20</sup> On this basis it would be possible to write,

$$\Lambda^0 = Ae^{-\frac{E}{RT}} \text{ or } \ln \Lambda^0 = \ln A - \frac{E}{RT} \quad (10)$$

where  $A$  is the frequency factor,  $R$  is universal gas constant, and  $E$  is the Arrhenius activation energy of transport processes.

A the plot of  $\ln \Lambda^0$  versus  $1/T$  for the potassium salts for all glycerol +  $\text{H}_2\text{O}$  mixtures gives  $E$  values from corresponding slopes<sup>21</sup> and are listed in Table 4.

A perusal of Table 4 shows that  $E$  increases as the concentration of glycerol increases in the mixture. It is well accepted that the activation of electrolytic conductance is almost identical with that for the viscous flow of the solvent; the constancy of  $E$  means that the positive temperature coefficient of ion conductance is roughly equal to the negative temperature coefficient of viscosity.<sup>22</sup>

The free energy change ( $\Delta G^0$ ) for association is calculated from the relation,<sup>23</sup>

$$\Delta G^0 = -RT \ln K_A \quad (11)$$

The heat of association ( $\Delta H^0$ ) is obtained by studying the association constant ( $K_A$ ) over a range of temperature by means of Van't Hoff's isochore, where  $\ln K_A^0$  values are plotted against  $1/T$  giving a straight line with slope  $-\Delta H^0/R$ . The negative  $\Delta H^0$  values obtained are found to decrease systematically with the concentration glycerol in the mixture.

The entropy change ( $\Delta S^0$ ) is calculated from the Gibbs-Helmholtz equation,

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \quad (12)$$

The values of these thermodynamic functions are given in Table 5.

#### 12.4. Conclusion

If we consider that from a rudimentary standpoint the ion-pair is formed with only the action of the Coulombic force in a continuum medium, the values of  $\Delta H^0$  and  $\Delta S^0$  of the ion-pair formation will be negative. Therefore, all the experimental values of  $\Delta H^0$  and  $\Delta S^0$  are negative for all potassium salts studied. The negative sign of  $\Delta H^0$  means that the association processes are exothermic.

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Table 1

Molar Conductances ( $\Lambda$ ), Densities ( $\rho$ ) and Molar Concentration ( $c$ ) of Various Potassium Salts in Glycerol (1) + Water (2)

Mixtures at Different Temperatures.

298.15 K		308.15 K			318.15 K			
$c \times 10^4$ (mol. dm <sup>-3</sup> )	$\rho \times 10^{-3}$ (kg. m <sup>-3</sup> )	$\Lambda \times 10^4$ (S. m <sup>2</sup> . mol <sup>-1</sup> )	$c \times 10^4$ (mol. dm <sup>-3</sup> )	$\rho \times 10^{-3}$ (kg. m <sup>-3</sup> )	$\Lambda \times 10^4$ (S. m <sup>2</sup> . mol <sup>-1</sup> )	$c \times 10^4$ (mol. dm <sup>-3</sup> )	$\rho \times 10^{-3}$ (kg. m <sup>-3</sup> )	$\Lambda \times 10^4$ (S. m <sup>2</sup> . mol <sup>-1</sup> )
$x_1 = 0.0213$								
<b>KCl</b>								
163.0	1.0209	96.9	162.5	1.0176	116.3	162.0	1.0146	138.2
253.6	1.0212	93.8	252.8	1.0180	112.6	252.0	1.0149	135.2
344.1	1.0216	91.5	343.0	1.0184	110.0	342.1	1.0153	132.5
434.7	1.0219	89.5	433.3	1.0187	107.8	432.1	1.0156	130.5
615.8	1.0226	85.7	613.8	1.0195	103.9	612.1	1.0164	126.8
706.3	1.0230	84.1	704.1	1.0199	102.4	701.9	1.0167	125.3
860.3	1.0238	81.8	857.7	1.0208	100.6	854.7	1.0173	123.0
<b>KBr</b>								
232.9	1.0218	102.5	232.1	1.0185	124.1	231.3	1.0153	143.0
349.3	1.0228	99.4	348.2	1.0195	121.0	347.1	1.0164	140.0
465.8	1.0238	97.2	464.3	1.0205	118.5	462.8	1.0173	137.4
582.2	1.0246	95.0	580.4	1.0214	116.4	578.6	1.0183	135.0
659.9	1.0252	93.6	657.8	1.0220	115.1	655.8	1.0189	133.8
698.7	1.0254	92.9	696.5	1.0223	114.3	694.4	1.0191	133.0
776.3	1.0264	91.5	774.0	1.0233	113.0	771.2	1.0197	131.6
<b>KI</b>								
197.8	1.0226	108.2	197.2	1.0193	126.6	196.1	1.0136	147.2
276.9	1.0235	105.9	276.0	1.0202	124.4	275.0	1.0150	145.0
395.6	1.0249	103.2	394.4	1.0217	121.8	393.3	1.0170	142.2
514.3	1.0262	101.0	512.8	1.0231	119.5	511.9	1.0190	139.8
633.0	1.0275	99.1	631.2	1.0245	117.6	629.0	1.0208	137.5



751.7	1.0290	97.3	749.4	1.0258	115.6	747.0	1.0226	136.0
830.87	1.0302	96.01	828.2	1.0269	114.26	825.6	1.0237	134.56
$x_1 = 0.0466$								
<b>KCl</b>								
185.1	1.0438	75.0	184.5	1.0405	91.8	183.92	1.0372	114.8
259.1	1.0442	72.7	258.1	1.0408	89.6	257.44	1.0375	112.4
370.1	1.0448	69.9	368.9	1.0413	86.5	367.68	1.0379	109.3
481.2	1.0453	67.8	479.6	1.0417	84.0	478.00	1.0384	106.7
592.2	1.0459	65.9	590.1	1.0422	82.1	588.51	1.0389	104.2
666.2	1.0464	64.8	663.7	1.0425	81.1	661.72	1.0393	102.6
740.3	1.0467	63.7	737.8	1.0429	79.9	735.53	1.0396	100.9
<b>KBr</b>								
183.6	1.0446	88.6	183.0	1.0412	97.8	182.5	1.0380	123.7
257.1	1.0452	84.7	256.3	1.0417	95.6	255.5	1.0385	121.3
367.3	1.0460	82.2	366.0	1.0425	92.9	364.9	1.0392	118.3
477.5	1.0468	80.1	475.9	1.0434	90.8	474.4	1.0401	115.6
587.7	1.0477	78.2	586.0	1.0441	89.0	584.2	1.0409	113.6
661.2	1.0483	76.8	658.9	1.0447	88.0	656.8	1.0413	112.3
734.6	1.0490	75.8	732.2	1.0457	87.1	729.9	1.0424	111.2
<b>KI</b>								
170.3	1.0454	91.9	169.7	1.0417	108.8	169.2	1.0385	130.8
238.5	1.0463	89.8	237.6	1.0428	106.8	236.8	1.0393	128.6
340.7	1.0474	87.5	339.5	1.0438	104.3	338.5	1.0405	125.8
442.9	1.0488	85.4	441.2	1.0450	102.3	439.8	1.0417	123.4
545.1	1.0499	83.8	543.2	1.0463	100.5	541.5	1.0429	121.3
647.3	1.0513	82.1	644.7	1.0470	98.8	642.9	1.0440	119.5
715.5	1.0520	81.0	713.4	1.0484	97.8	711.1	1.0451	118.5
$x_1 = 0.0773$								
<b>KCl</b>								
171.6	1.0682	53.0	170.9	1.0643	68.4	170.4	1.0607	83.2
240.2	1.0685	51.4	239.3	1.0645	66.5	238.5	1.0610	81.1

343.2	1.0690	49.6	341.9	1.0649	64.2	340.8	1.0615	78.5	
446.1	1.0694	48.0	444.5	1.0658	62.1	443.9	1.0620	76.6	
549.1	1.0700	46.5	546.9	1.0657	60.6	545.9	1.0624	74.7	
617.7	1.0702	45.3	615.2	1.0660	59.6	613.5	1.0627	73.6	
686.4	1.0705	44.5	683.8	1.0664	58.5	681.6	1.0630	72.0	
<b>KBr</b>									
168.8	1.0685	64.2	168.2	1.0648	80.6	167.9	1.0627	97.0	
239.1	1.0691	62.6	238.4	1.0855	78.5	237.8	1.0631	95.0	
337.6	1.0699	60.6	336.5	1.0661	76.5	335.6	1.0634	92.8	
436.1	1.0706	59.0	434.4	1.0670	74.6	433.1	1.0638	90.7	
548.7	1.0715	57.4	546.8	1.0678	72.9	544.9	1.0643	88.6	
619.0	1.0720	56.5	617.1	1.0686	71.6	614.7	1.0646	87.4	
568.3	1.0723	55.8	666.2	1.0690	70.8	663.7	1.0649	86.5	
<b>KI</b>									
172.4	1.0693	71.0	1471.8	1.0654	87.5	171.3	1.0620	101.5	
241.4	1.0701	69.4	240.6	1.0665	85.4	239.8	1.0632	99.6	
344.8	1.0712	67.3	343.6	1.0674	83.1	342.4	1.0638	97.2	
448.3	1.0722	65.7	447.0	1.0691	81.2	445.2	1.0647	95.3	
551.7	1.0732	64.2	550.5	1.0708	79.6	548.4	1.0666	93.4	
620.7	1.0742	63.2	619.1	1.0714	78.6	616.4	1.0667	92.3	
689.7	1.0754	62.4	687.2	1.0716	77.5	685.2	1.0684	91.1	

Table 2.  
 Values of Density ( $\rho$ ), Viscosity ( $\eta$ ) and Dielectric Constant ( $\epsilon$ ) of Glycerol (1) + Water (2) Mixtures at Various Temperatures.

Glycerol (Mass %)	Property	298.15 K	308.15 K	318.15 K
10	$\rho \times 10^{-3}$ (kg. m <sup>-3</sup> )	1.0200 <sup>a</sup>	1.0074 <sup>a</sup> (1.007 <sup>b</sup> )	0.9940 <sup>a</sup>
		(1.020 <sup>b</sup> )	0.9110 <sup>a</sup> (0.911 <sup>b</sup> )	0.6700 <sup>a</sup>
	$\eta \times 10^3$ (Pa. s)	1.1530 <sup>a</sup>	72.19 <sup>b</sup>	68.56 <sup>b</sup>
		(1.153 <sup>b</sup> )		
$\epsilon$	75.70 <sup>b</sup>			
20	$\rho \times 10^{-3}$ (kg. m <sup>-3</sup> )	1.0430 <sup>a</sup>	1.0380 <sup>a</sup>	1.0330 <sup>a</sup>
		1.5342 <sup>b</sup>	1.2087 <sup>a</sup>	0.7960 <sup>a</sup>
	$\eta \times 10^3$ (Pa. s)	72.0 <sup>a</sup>	69.36 <sup>a</sup>	66.73 <sup>a</sup>
$\epsilon$				
30	$\rho \times 10^{-3}$ (kg. m <sup>-3</sup> )	1.0700 <sup>a</sup>	1.0572 <sup>a</sup> (1.057 <sup>b</sup> )	1.0393 <sup>a</sup>
		(1.070 <sup>b</sup> )	1.6370 <sup>b</sup>	1.1425 <sup>a</sup>
	$\eta \times 10^3$ (Pa. s)	2.1570 <sup>b</sup>	66.53 <sup>b</sup>	63.12 <sup>b</sup>
		70.00 <sup>b</sup>		
$\epsilon$				

<sup>a</sup>Calculated values, <sup>b</sup> from Ref 16 and 24.

**Conductometric Study of Some Metal Halides in Glycerol + Water Mixtures**

Table 3.

Derived Conductivity Parameters for Some Potassium Salts in Glycerol (1) + H<sub>2</sub>O (2) at 298.15 to 318.15 K.

Glycerol (Mass %)	T (K)	$\Lambda^0 \times 10^4$ (S.m <sup>2</sup> . mol <sup>-1</sup> )	$K_A$ (dm <sup>-3</sup> . mol <sup>-1</sup> )	R (Å)	$\sigma$
KCl					
10	298.15	105.73	5.48	6.31	0.10
	308.15	125.01	4.47	6.32	0.40
	318.15	147.09	3.28	6.33	0.19
20	298.15	84.04	7.17	6.38	0.11
	308.15	101.26	5.73	6.39	0.19
	318.15	125.81	5.00	6.40	0.21
30	298.15	60.20	8.48	6.46	0.19
	308.15	76.40	7.31	6.48	0.06
	318.15	91.99	6.33	6.50	0.20
KBr					
10	298.15	112.77	4.35	6.45	0.13
	308.15	134.46	3.37	6.46	0.09
	318.15	154.11	2.93	6.47	0.06
20	298.15	95.51	5.48	6.52	0.12
	308.15	105.97	4.39	6.53	0.19
	318.15	133.30	3.89	6.54	0.17
30	298.15	70.78	6.24	6.60	0.05
	308.15	88.26	5.58	6.62	0.12
	318.15	105.45	4.79	6.64	0.11
KI					
10	298.15	116.81	3.77	6.66	0.12
	308.15	135.60	3.10	6.67	0.12
	318.15	156.69	2.63	6.68	0.15
20	298.15	99.73	4.79	6.73	0.07
	308.15	116.83	3.83	6.74	0.08
	318.15	139.91	3.50	6.75	0.12
30	298.15	77.70	5.40 (6)	6.81	0.04
	308.15	95.05	4.89	6.83	0.14
	318.15	109.75	4.26	6.85	0.09

Table 4.  
Values of Activation Energy ( $E$ ) and Walden Products ( $\Lambda^0 \eta^0$ ) of Some Potassium Salts in Glycerol (1) + H<sub>2</sub>O (2) Mixtures at Various Temperatures.

Glycerol (Mass %)	$E$ (kJ. mol <sup>-1</sup> )	$\Lambda^0 \eta^0 \times 10^7$ (S.m <sup>2</sup> .mol <sup>-1</sup> .Pa. s)		
		298.15 K	308.15 K	318.15 K
KCl				
10	13.00	121.91	113.89	98.56
20	15.74	128.94	122.39	100.15
30	16.96	129.46	125.07	105.10
KBr				
10	12.22	130.03	122.50	103.26
20	13.43	146.53	128.09	106.11
30	15.77	152.67	144.48	120.48
KI				
10	11.42	134.69	123.54	104.99
20	13.38	153.01	141.21	111.37
30	13.80	167.60	155.60	125.39

(6)

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Table 5.

Thermodynamic Functions for Association of Potassium Salts in Glycerol (1) + H<sub>2</sub>O (2) Mixtures at Various Temperatures

Glycerol (Mass %)	<i>T</i> (K)	$-\Delta H^0$ (kJ. mol <sup>-1</sup> )	$-\Delta G^0$ (kJ. mol <sup>-1</sup> )	$-\Delta S^0$ (J. K <sup>-1</sup> . mol <sup>-1</sup> )
		KCl		
10	298.15	20.04	4.21	53.12
	308.15	20.04	3.83	52.63
	318.15	20.04	3.14	53.14
20	298.15	14.21	4.88	31.31
	308.15	14.21	4.47	31.62
	318.15	14.21	4.26	31.28
30	298.15	11.42	5.30	20.54
	308.15	11.42	5.09	20.55
	318.15	11.42	4.88	20.57
		KBr		
10	298.15	15.41	3.64	39.50
	308.15	15.41	3.11	39.94
	318.15	15.41	2.84	39.53
20	298.15	12.94	4.21	29.30
	308.15	12.94	3.79	29.71
	318.15	12.94	3.59	29.40
30	298.15	10.22	4.54	19.06
	308.15	10.22	4.40	19.00
	318.15	10.22	4.14	19.12
		KI		
10	298.15	14.19	3.29	36.58
	308.15	14.19	2.90	36.66
	318.15	14.19	2.56	36.57
20	298.15	12.66	3.88	29.46
	308.15	12.66	3.44	29.94
	318.15	12.66	3.31	29.40
30	298.15	9.43	4.18	17.62
	308.15	9.43	4.06	17.44
	318.15	9.43	3.83	17.61