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Conductometric Study of Some Metal Halides in Glycerol + Water Mixtures

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Electrolytic conductivities of potassium halides, KX (X = Cl^-, Br^-, I^-) have been investigated in 10, 20, and 30 mass% glycerol + H_2O mixtures at 298.0, 308.0, and 318.0 K. The conductance data have been analyzed by the Fuoss-conductance–concentration equation in terms of the limiting molar conductance (Λ^0), the association constant (K_A), and the distance of closest approach of ion (R). The association constant (K_A) tends to increase in the order: 10 mass% < 20 mass% < 30 mass% glycerol + water mixtures, while it decreases with temperature. Thermodynamic parameters ΔH^0, ΔG^0, and ΔS^0 are obtained and discussed. Also, Walden products ($\Lambda^0\eta$) are reported. The results have been interpreted in terms of ion–solvent interactions and structural changes in the mixed solvents.

KEY WORDS: association constant; density; glycerol; limiting conductance; potassium bromide; potassium chloride; potassium iodide; thermodynamic parameters ΔH^0, ΔG^0, and ΔS^0; Walden product.

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 [1, 2]. Shehata et al. [3, 4] studied the electrical conductivities of $Ba(NO_3)_2$ and $Sr(NO_3)_2$ in glycerol + H_2O mixtures to determine the nature of ionic associations and mobility of ions in this mixed solvent system. In the present study, an attempt has

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been made to ascertain the nature of ion–solvent interactions of potassium halides (chloride, bromide, and iodide) in glycerol + H_2O mixtures using the conductometric technique. Thermodynamic parameters are also evaluated and discussed.

2. EXPERIMENTAL

Potassium metal salts were of puris or purum grade (Fluka), quoted as 99.5% pure and were purified as described earlier [5, 6]. Water was doubly-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 [7].

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 [8].

The densities (ρ) were measured with an Ostwald–Sprengel type pycnometer having a bulb volume of $25\,\mathrm{cm}^3$ and a capillary with an internal diameter of about 0.1 cm. The pycnometer was calibrated at 298.0, 308.0, and 318.0 K using doubly distilled water and benzene. The pycnometer with the test solution was equilibrated in a water bath maintained at ±0.005 K of the desired temperature by means of a mercury-in-glass thermoregulator, 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 $\pm 3 \times 10^{-3}\,\mathrm{g \cdot cm^{-3}}$. Details have been described earlier [9–11].

The viscosities were measured by means of a suspended level Ubbelohde viscometer at the desired temperature (uncertainty of ±0.005 K). The precision of the viscosity measurement was ±0.005 mPa·s. Details have been described earlier [12, 13].

Conductance measurements were carried out with a Systonic-306 conductivity bridge using a dip-type cell (cell constant $= 0.1\,\mathrm{cm}^{-1}$) with an uncertainty of 0.01%. The cell was calibrated by the method of Lind and co-workers [14] using aqueous potassium chloride solutions. Measurements were made as described earlier [15].

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_2O mixture were 5.08×10^{-5}, 6.63×10^{-5}, and $8.18 \times 10^{-5}\,\mathrm{S \cdot cm^{-1}}$ at 298.0, 308.0, and

318.0 K, respectively. The concentrations of measured solutions were in the range of 6.86×10^{-3} to 8.68×10^{-2} mol·dm^{-3}.

3. DISCUSSION

Molar conductances (Λ), densities (ρ), and molar concentrations (c) are given in Table I in different solvent mixtures at 298.0, 308.0, and 318.0 K. The solvent properties of glycerol + H_2O mixtures are given in Table II. Dielectric constants of the solvent mixture were obtained by extrapolation of D (dielectric constant) versus W (the mass of glycerol in the aqueous mixtures) plots; the original values were taken from the work of Akerlof [16].

The conductance data have been analyzed by the Fuoss-conductance–concentration equation [17, 18]. For a given set of conductivity values ($c_j, A_j, j = 1, \ldots, n$), three adjustable parameters, the limiting molar conductivity (Λ^0), the association constant (K_A), and the distance of closest approach of ions (R) are derived from the following set of equations:

$$\Lambda = P[\Lambda^0(1 + R_X) + E_L] \tag{1}$$

$$P = 1 - \alpha(1 - \gamma) \tag{2}$$

$$\gamma = 1 - K_A c \gamma^2 f^2 \tag{3}$$

$$-\ln f = \beta\kappa / 2(1 + \kappa R) \tag{4}$$

$$\beta = e^2/(D k_B T) \tag{5}$$

$$K_A = K_R/(1 - \alpha) = K_R(1 + K_S) \tag{6}$$

where R_X is the relaxation field effect, E_L is the electrophoretic countercurrent, K^{-1} is the radius of the ion atmosphere, D is the dielectric constant of the solvent, e is the electron charge, k_B is the Boltzmann constant, γ is the fraction of solute present as an unpaired ion, c is the molarity of the solution, f is the activity coefficient, T is the absolute temperature, and β is twice the Bjerrum distance.

The computations were performed using a program suggested by Fuoss. The initial Λ^0 values for the iteration procedure were obtained from Shedlovsky extrapolation of the data. Input for the program is the set ($c_j, A_j; j = 1, \ldots., n$), n, D, η, T, initial values of Λ^0, and an instruction to cover a preselected range of R values.

In practice, calculations are performed by finding the values of Λ^0 and α which minimize the standard deviation:

$$\delta^2 = \sum[\Lambda_j(\text{calcd}) - \Lambda_j(\text{obsd})]^2/(n - 2) \tag{7}$$

Table I. Molar Conductances (Λ), Densities (ρ), and Molar Concentration (*c*) of Various Potassium Salts in Glycerol (1) + Water (2) Mixtures at Different Temperatures

298.0 K			308.0 K			318.0 K		
$c \times 10^4$ (mol·dm^{-3})	ρ (g·cm^{-3})	Λ (S·cm^2·mol^{-1})	$c \times 10^4$ (S·cm^2·mol^{-1})	ρ (mol·dm^{-3})	Λ (g·cm^{-3})	$c \times 10^4$ (mol·dm^{-3})	ρ (g·cm^{-3})	Λ (S·cm^2·mol^{-1})
				KCl $x_1^a = 0.021256$				
163.0	1.02089	96.93	162.5	1.01762	116.31	162.0	1.01461	138.24
253.6	1.02123	93.88	252.8	1.01800	112.60	252.0	1.01491	135.26
344.1	1.02158	91.58	343.0	1.01836	110.06	342.1	1.01531	132.54
434.7	1.02194	89.56	433.3	1.01875	107.88	432.1	1.01561	130.54
615.8	1.02262	85.76	613.8	1.01955	103.98	612.1	1.01641	126.87
706.3	1.02305	84.14	704.1	1.01994	102.44	701.9	1.01668	125.36
860.3	1.02376	81.87	857.7	1.02080	100.62	854.7	1.01730	123.06
				KBr $x_1^a = 0.021256$				
232.9	1.02182	102.58	232.1	1.01849	124.11	231.3	1.01534	143.08
349.3	1.02284	99.48	348.2	1.01954	121.01	347.1	1.01640	140.01
465.8	1.02382	97.21	464.3	1.02053	118.51	462.8	1.01730	137.44
582.2	1.02460	95.02	580.4	1.02143	116.40	578.6	1.01830	135.06
659.9	1.02525	93.68	657.8	1.02203	115.10	655.8	1.01894	133.80
698.7	1.02544	92.98	696.5	1.02231	114.36	694.4	1.01913	133.01
776.3	1.02644	91.58	774.0	1.02331	113.02	771.2	1.01970	131.67
				KI $x_1^a = 0.021256$				
197.8	1.02264	108.23	197.2	1.01932	126.68	196.1	1.01358	147.22
276.96	1.02354	105.98	276.0	1.02017	124.41	275.0	1.01503	145.06
395.65	1.02492	103.26	394.4	1.02170	121.87	393.3	1.01703	142.22
514.35	1.02618	101.06	512.8	1.02312	119.54	511.9	1.01903	139.88
633.04	1.02752	99.16	631.2	1.02450	117.60	629.0	1.02083	137.54
751.70	1.02900	97.36	749.4	1.02579	115.62	747.0	1.02258	136.05
830.87	1.03019	96.01	828.2	1.02686	114.26	825.6	1.02366	134.56

				KCl $x_1^a = 0.046589$				
185.1	1.04385	75.09	184.5	1.04046	91.88	183.92	1.03719	114.85
259.1	1.04420	72.76	258.08	1.04080	89.68	257.44	1.03750	112.42
370.1	1.04479	69.98	368.9	1.04126	86.54	367.68	1.03795	109.35
481.2	1.04528	67.81	479.6	1.04171	84.06	478.00	1.03842	106.74
592.2	1.04588	65.97	590.1	1.04219	82.14	588.51	1.03893	104.21
666.2	1.04637	64.89	663.7	1.04253	81.11	661.72	1.03934	102.60
740.3	1.04676	63.77	737.8	1.04293	79.99	735.53	1.03964	100.94
				KBr $x_1^a = 0.046589$				
183.66	1.04464	86.88	183.05	1.04116	97.84	182.5	1.03803	123.71
257.12	1.04522	84.75	256.30	1.04173	95.64	255.5	1.03851	121.30
367.31	1.04602	82.24	366.09	1.04253	92.94	364.9	1.03923	118.30
477.50	1.04679	80.12	475.96	1.04342	90.89	474.4	1.04015	115.64
587.70	1.04766	78.21	586.04	1.04412	89.01	584.2	1.04088	113.68
661.20	1.04832	76.83	658.94	1.04474	88.02	656.8	1.04130	112.32
734.62	1.04904	75.85	732.27	1.04568	87.14	729.9	1.04241	111.25
				KI $x_1^a = 0.046589$				
170.36	1.04540	91.96	169.75	1.04167	108.87	169.22	1.03846	130.85
238.50	1.04631	89.89	237.62	1.04281	106.89	236.83	1.03933	128.65
340.71	1.04744	87.54	339.54	1.04383	104.34	338.50	1.04050	125.87
442.93	1.04876	85.47	441.26	1.04505	102.36	439.85	1.04172	123.46
545.14	1.04995	83.88	543.23	1.04627	100.54	541.50	1.04294	121.35
647.36	1.05128	82.12	644.70	1.04697	98.87	642.90	1.04405	119.58
715.50	1.05203	81.06	713.40	1.04840	97.80	711.19	1.04514	118.54
				KCl $x_1^a = 0.07729$				
171.61	1.06822	53.02	170.98	1.06431	68.45	170.41	1.06075	83.21
240.25	1.06855	51.44	239.30	1.06456	66.59	238.55	1.06104	81.14
343.21	1.06902	49.68	341.90	1.06494	64.21	340.87	1.06156	78.58

Table I. *(Continued)*

298.0 K			308.0 K			318.0 K		
$c \times 10^4$ (mol·dm^{-3})	ρ (g·cm^{-3})	Λ (S·cm^2·mol^{-1})	$c \times 10^4$ (S·cm^2·mol^{-1})	ρ (mol·dm^{-3})	Λ (g·cm^{-3})	$c \times 10^4$ (mol·dm^{-3})	ρ (g·cm^{-3})	Λ (S·cm^2·mol^{-1})
446.17	1.06940	48.01	444.50	1.06538	62.18	443.96	1.06203	76.60
549.14	1.06997	46.58	546.98	1.06576	60.64	545.92	1.06248	74.70
617.78	1.07019	45.36	615.29	1.06604	59.60	613.51	1.06278	73.60
686.42	1.07050	44.58	683.82	1.06644	58.59	681.66	1.06306	72.04
KBr $x_1^a = 0.07729$								
168.84	1.06851	64.25	168.23	1.06480	80.67	167.90	1.06270	97.02
239.19	1.06916	62.64	238.40	1.06550	78.58	237.82	1.06310	95.00
337.68	1.06990	60.61	336.50	1.06610	76.55	335.63	1.06340	92.84
436.17	1.07069	59.01	434.44	1.06700	74.65	433.16	1.06380	90.76
548.73	1.07159	57.41	546.80	1.06780	72.90	544.99	1.06430	88.62
619.08	1.07205	56.54	617.10	1.06860	71.66	614.76	1.06460	87.45
668.33	1.07239	55.84	666.20	1.06900	70.84	663.70	1.06490	86.54
KI $x_1^a = 0.07729$								
172.43	1.06932	71.05	171.80	1.06548	87.58	171.3	1.06205	101.56
241.40	1.07013	69.44	240.60	1.06659	85.41	239.8	1.06329	99.64
344.85	1.07125	67.38	343.60	1.06748	83.12	342.4	1.06380	97.21
448.31	1.07226	65.74	447.00	1.06917	81.25	445.2	1.06474	95.31
551.76	1.07326	64.23	550.50	1.07086	79.64	548.4	1.06667	93.47
620.73	1.07424	63.26	619.14	1.07148	78.62	616.4	1.06674	92.32
689.70	1.07549	62.48	687.20	1.07161	77.54	685.2	1.06844	91.12

[a] x_1 is the mole fraction of glycerol.

Table II. Values of Density, Viscosity, and Dielectric Constant of Glycerol (1) + Water (2) Mixtures at Various Temperatures

Glycerol (mass%)	Property	298.0 K	308.0 K	318.0 K
10	Density ($g \cdot cm^{-3}$)	1.02001[a] (1.020[b])	1.00742[a] (1.007[b])	0.99403[a]
	Viscosity ($mPa \cdot s$)	1.15303[a] (1.153[b])	0.91104[a] (0.911[b])	0.67004[a]
	Dielectric constant	75.70[b]	72.19[b]	68.56[b]
20	Density ($g \cdot cm^{-3}$)	1.04300[a]	1.03801[a]	1.03304[a]
	Viscosity ($mPa \cdot s$)	1.53423[b]	1.20872[a]	0.79601[a]
	Dielectric constant	72.0[a]	69.36[a]	66.73$^{=}$
30	Density ($g \cdot cm^{-3}$)	1.07003[a] (1.070[b])	1.05722[a] (1.057[b])	1.03926[a]
	Viscosity ($mPa \cdot s$)	2.15700[b]	1.6370[b]	1.14250[a]
	Dielectric constant	70.00[b]	66.53[b]	63.12[b]

[a] Calculated values.
[b] From Refs. [16, 24].

for a sequence of R values and then plotting δ gainst R; the best-fit R corresponds to the minimum of the $\delta - R$ versus R curve. So, approximate runs are made over a fairly wide range of R values using 0.1 increments to locate the minimum, but no significant minima were found in the $\delta - R$ curves for all the salts studied here; thus, R values are assumed to be $R = a + d$, where a is the sum of the crystallographic radii of the ions and d is the average distance corresponding to the side of a cell occupied by a solvent molecule. The distance d is given by

$$d((\text{Å})) = 1.183(M/\rho)^{1/3} \tag{8}$$

where M is the molar mass of the solvent and ρ is its density. For mixed solvents, M is replaced by the mole fraction average molar mass (M_{av}) which is given by

$$M_{\text{av}} = M_1 M_2 / (W_1 M_2 + W_1 M_2) \tag{9}$$

where W_1 is the mass fraction of the first component of molar mass M_1. The values of Λ^0, K_A, and R obtained by this procedure are reported in Table III.

Inspection of the data in Table III shows that the values of Λ^0 of all salts decrease as the concentration of glycerol in the aqueous mixtures increases. But as the temperature increases, Λ^0 values increase for all glycerol + H_2O mixtures. The trends in Λ^0 can be discussed through another characteristic function called the Walden product, $\Lambda^0\eta$. Although Λ^0 decreases as the concentration of glycerol increases, $\Lambda^0\eta$ (Table IV)

Table III. Derived Conductivity Parameters for Potassium Salts in Glycerol (1) + H_2O(2) from 298.0 to 318.0 K

Glycerol (mass%)	T(K)	Λ^0 (S·cm^2·mol^{-1})	K_A (dm^{-3}·mol^{-1})	R (Å)	δ
		KCl			
10	298.0	105.73 (± 0.10)	5.48	6.31	0.10
	308.0	125.01 (± 0.40)	4.47	6.32	0.40
	318.0	147.09 (± 0.19)	3.28	6.33	0.19
20	298.0	84.04 (± (0.11)	7.17	6.38	0.11
	308.0	101.26 (± 0.19)	5.73	6.39	0.19
	318.0	125.81 (± 0.21)	5.00	6.40	0.21
30	298.0	60.20 (± 0.19)	8.48	6.46	0.19
	308.0	76.40 (± 0.06)	7.31	6.48	0.06
	318.0	91.99 (± 0.20)	6.33	6.50	0.20
		KBr			
10	298.0	112.77 (± 0.13)	4.35	6.45	0.13
	308.0	134.46 (± 0.09)	3.37	6.46	0.09
	318.0	154.11 (± 0.06)	2.93	6.47	0.06
20	298.0	95.51 (± 0.12)	5.48	6.52	0.12
	308.0	105.97 (± 0.19)	4.39	6.53	0.19
	318.0	133.30 (± 0.17)	3.89	6.54	0.17
30	298.0	70.78 (± 0.05)	6.24	6.60	0.05
	308.0	88.26 (± 0.12)	5.58	6.62	0.12
	318.0	105.45 (± 0.11)	4.79	6.64	0.11
		KI			
10	298.0	116.81 (± 0.12)	3.77	6.66	0.12
	308.0	135.60 (± 0.12)	3.10	6.67	0.12
	318.0	156.69 (± 0.15)	2.63	6.68	0.15
20	298.0	99.73 (± 0.07)	4.79	6.73	0.07
	308.0	116.83 (± 0.08)	3.83	6.74	0.08
	318.0	139.91 (± 0.12)	3.50	6.75	0.12
30	298.0	77.70 (± 0.04)	5.40	6.81	0.04
	308.0	95.05 (± 0.14)	4.89	6.83	0.14
	318.0	109.75 (± 0.09)	4.26	6.85	0.09

increases due to the increase of the viscosity (η). $\Lambda^0\eta$ decreases with an increase in temperature at 298.0, 308.0, and 318.0 K for all glycerol + H_2O mixtures. The decrease in $\Lambda^0\eta$ is small. The decrease in $\Lambda^0\eta$ with temperature, which is common in aqueous solutions [19], 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 III, we see that Λ^0 of potassium salts of common cations follow the sequence: Cl$^- < Br^- < I^-$. Furthermore, Λ^0 of the studied electrolyte is enhanced in the following order: KI > KBr > KCl. The sizes

Table IV. Values of Activation Energy (E) and Walden Products ($\Lambda^0\eta$) of Potassium Salts in Glycerol (1) + H_2O (2) Mixtures at Various Temperatures

		$\Lambda^0\eta \times 10^3$ (S·cm^2·mol^{-1}·Pa·s)		
Glycerol (mass%)	E (kJ·mol^{-1})	298.0	308.0	318.0
	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

of these anions as they exist in solution follow the order: $Cl^- > Br^- > I^-$. This shows that potassium halides with Cl^- are the most solvated and those with I^- are the least solvated one in all concentrations of glycerol + H_2O mixtures. A similar result [6] 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 the rate of movement, it seems reasonable to treat the conductance in a manner analogous to that employed for other processes taking place at a definite rate which increases with temperature [20]. On this basis it would be possible to write:

$$\Lambda^0 = A\ \mathrm{e}^{-E/RT} \quad \text{or}$$
$$\ln \Lambda^0 = \ln A - E/RT \tag{10}$$

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

Thus, from the plot of log Λ^0 versus $1/T$ for the potassium salts for all glycerol + H_2O mixtures, E values have been computed from the slope [21] and are recorded in Table IV.

Table V. Thermodynamic Functions for Association of Potassium Salts in Glycerol (1) + H_2O (2) Mixtures at Various Temperatures

Glycerol (mass%)	T (K)	$-\Delta H^0$ (kJ·mol^{-1})	$-\Delta G^0$ (kJ·mol^{-1})	$-\Delta S^0$ (J·K^{-1}·mol^{-1})
		KCl		
	298.0	20.04	4.21	53.12
10	308.0	20.04	3.83	52.63
	318.0	20.04	3.14	53.14
	298.0	14.21	4.88	31.31
20	308.0	14.21	4.47	31.62
	318.0	14.21	4.26	31.28
	298.0	11.42	5.30	20.54
30	308.0	11.42	5.09	20.55
	318.0	11.42	4.88	20.57
		KBr		
	298.0	15.41	3.64	39.50
10	308.0	15.41	3.11	39.94
	318.0	15.41	2.84	39.53
	298.0	12.94	4.21	29.30
20	308.0	12.94	3.79	29.71
	318.0	12.94	3.59	29.40
	298.0	10.22	4.54	19.06
30	308.0	10.22	4.40	19.00
	318.0	10.22	4.14	19.12
		KI		
	298.0	14.19	3.29	36.58
10	308.0	14.19	2.90	36.66
	318.0	14.19	2.56	36.57
	298.0	12.66	3.88	29.46
20	308.0	12.66	3.44	29.94
	318.0	12.66	3.31	29.40
	298.0	9.43	4.18	17.62
30	308.0	9.43	4.06	17.44
	318.0	9.43	3.83	17.61

A perusal of Table IV 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 [22].

The free energy charge (ΔG^0) for association is calculated from the relation [23]:

$$\Delta G^0 = -RT \ln K_A \tag{11}$$

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

The entropy change (ΔS^0) is calculated from the Gibbs–Helmholtz equation:

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \tag{12}$$

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

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 ΔH^0 nd ΔS^0 of the ion-pair formation will be negative. Therefore, all the experimental values of ΔH^0 and ΔS^0 are negative for all potassium salts studied here (Table V). The negative sign of ΔH^0 means that the association processes are exothermic.

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