ELECTRICAL CONDUCTANCE OF SOME SODIUM AND POTASSIUM SALTS IN METHANOL AT 25 °C

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Abstract:
The electrical conductivities of solutions of some sodium and potassium salts (KI, KSCN, KCH_3COO, NaI, NaBr and $NaCH_3COO$) in methanol have been measured in concentration range (0.001-1 molar) at 25 °C. Values of molar conductivity at infinite dilution were obtained by extrapolation using the conductance equation of Onsager. The conductance data have been analyzed by the Fuoss conductance-concentration equation in terms of the limiting molar conductance ($\Lambda°$), the association constant (K_A), and the distance of closest approach of ions (R). The results have been interpreted in terms of ion-ion and ion-solvent interactions.

1. Introduction:

Electrical conductivity is one of the transport properties more frequently requested by chemist and engineers dealing with electrolyte solutions. Electrochemist has often used the very accurate conductivity data, which can be obtained from dilute systems to gain insight in to the structure of electrolyte solutions. It has been applied to monitor the purity of solvents to develop high-energy batteries [1].

Extensive studies on electrical conductivities in organic solvents have been performed in recent years to examine the nature and magnitude of ion-ion and ion-solvent interactions. Such solvent properties as the viscosity and the relative permittivity have also been taken into consideration, which help determine the extent of ion association and the solute-solvent interactions. The present study deals with methanol, a dipolar aprotic solvent. Methanol is known to be extensively self-associated through hydrogen bonding in the pure state [2].

In this work, we reported the molar conductivities of KI, KSCN, KCH_3COO, NaBr, NaI and $NaCH_3COO$ in concentration range (0.01-1 molar) in methanol solutions at 25 °C. The molar conductances at infinite dilution were obtained by extrapolation using the conductance equation of Onsager [3]. The conductance data have been analyzed by the Fuoss conductance-concentration equation [4] in terms of the limiting molar conductance ($\Lambda°$), the association constant (K_A), and distance of closet approach of ions (R).

2. Experimental Section

2.1. Materials. The salts and methanol obtained from Merck. They were all suprapure reagents (KI, GR, min 99.5; KSCN, GR, min 99%; KCH_3COO, GR, min 99.5%; NaI, GR, min 99.8%,NaBr, GR, min 99.5%, $NaCH_3COO$, GR, min 99.5%; methanol, GR, min 99.8%;). The salts were used without further purification and were dried in an electrical oven at about 120°C for 24 h prior to use. The purity as checked by gas chromatography was found to be better than 99.8% for methanol.

2.2. Apparatus and procedure. Conductance measurements were carried out on a Jenway model 4320 conduct meter using a glass cell (cell constant = 0.96 cm^{-1}) with an accuracy of

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0.01%. The cell was calibrated by the method of Lind and his co-workers [5] using aqueous potassium chloride solutions. Measurements were made in an water bath maintained at (25.0±0.005) °C. Several independent solutions were prepared, and conductance measurements were performed with each of these to ensure the reproducibility of the results.

3. Results

The Onsager limiting equation describing the concentration dependence of the molar conductivity is given by

$$\Lambda=\Lambda^{\circ}-(A\Lambda^{\circ}+B)c^{1/2} \tag{1}$$

A and B are the usual Onsager coefficients given, in SI units, by

$$A=\frac{N_A^{1/2}e^3}{12(1+2^{1/2})\pi(\varepsilon_0\varepsilon_r k_B T)^{3/2}} \tag{2}$$

$$B=\left[\frac{2e^6N_A^3}{9\pi^2\varepsilon_0\varepsilon_r k_B T\eta^2}\right]^{1/2} \tag{3}$$

N_A is the Avogadro constant, e is the proton charge, ε_0 is the permittivity of vacuum, ε_r is the relative permittivity of the solvent, k_B is the Boltzmann's constant, T is the absolute temperature, and η is the solvent viscosity. The relative permittivity ε_r and the viscosity for methanol at 25 °C were 32.63 and 0.542 mPa·s, respectively [1]. When replacing A and B, in equation 1, by their numerical values, the Onsager expression becomes

$$\Lambda/\mathrm{S\ m^2\ mol^{-1}}=\Lambda^{\circ}-(0.02705\Lambda^{\circ}+4.855\times10^{-7})(c/\mathrm{mol\ m^{-3}})^{1/2} \tag{4}$$

Molar conductance (Λ) of methanol electrolyte solutions as a function of molar concentration (*c*) are given in Table 1 at 25 °C. The values of Λº obtained through this method for KI, KSCN, KCH_3COO, NaI, NaBr and $NaCH_3COO$ in methanol solutions, are included in Table 1.

The conductance data have been analyzed by the Fuoss conductance-concentration equation [3] in terms of association constants (K_A), limiting conductivities (Λ°), and distance of closet approach of ions (R).

In the Fuoss conductance-concentration equation [3] for a given set of conductivity values (c_j, Λ_j; j=1... *n*), three adjustable parameters, the limiting molar conductivity (Λ°), the association constant (K_A), and the distance of closest approach of ions (R), are derived from the following set of equations:

$$\Lambda=p[\Lambda^{\circ}(1+R_x)+E_L \tag{5}$$

$$p=1-\alpha(1-\gamma) \tag{6}$$

$$\gamma=1-K_Ac\gamma^2f^2 \tag{7}$$

$$-\ln f=\beta k/2(1+kR) \tag{8}$$

$$\beta=e^2/Dk_BT \tag{9}$$

$$K_A=K_R/(1-\alpha)=K_R(1+K_S) \tag{10}$$

where R_x is the relaxation field effect, E_L is the electrophoretic countercurrent, k is the radius of the ion atmosphere, D is the relative permittivity of the solvent, e is the proton charge, k_B is the Boltzmann constant, γ is the fraction of solute present as 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 on a computer using the program suggested by Fuoss. The initial Λ° values for the iteration procedure were obtained from Shedlovsky extrapolation of the data. Input for the program is the set (c_j, Λ_j; j = 1... n), n, D, η ,T, initial value of Λ°, and an instruction to cover a reselected range of R values.

Table 1. Molar conductance, Λ, of NaI, NaBr and $NaCH_3COO$ in methanol as a function of molar concentration c at 25 °C.

Salt	C / (mol dm^{-3})	Λ/ (μS m^2 ·mol^{-1})	Λ°/ (μS m^2 ·mol^{-1})
NaI	0.0010	108.432	110.295
	0.0100	91.666	
	0.0500	73.572	
	0.1000	67.314	
	0.2000	58.857	
	0.3000	53.030	
	0.4000	50.140	
	0.5000	45.872	
	0.7000	40.857	
	0.9000	36.791	
	1.0000	35.992	
NaBr	0.0010	89.520	90.679
	0.0100	79.090	
	0.0500	65.124	
	0.1000	57.138	
	0.2000	50.649	
	0.3000	45.382	
	0.4000	41.380	
	0.5000	38.384	
	0.7000	34.275	
	0.9000	31.031	
$NaCH_3COO$	0.0010	81.456	83.735
	0.0100	60.946	
	0.0500	48.996	
	0.1000	37.074	
	0.2000	14.745	
	0.4000	9.004	
	0.6000	7.715	
	0.8000	11.126	
KI	0.0012	145.421	156.810
	0.0025	144.71	
	0.0050	121.123	
	0.0100	109.234	
	0.2500	58.644	
	0.5000	49.52	
	0.7500	43.638	
KSCN	0.0012	122.458	127.244
	0.0025	112.07	
	0.0050	102.499	
	0.0100	92.242	
	0.0625	76.368	
	0.1250	68.289	
	0.2500	57.646	
	0.5000	48.752	
	0.7500	43.638	
KCH_3COO	0.0012	91.738	99.438
	0.0025	84.038	
	0.0050	78.499	
	0.0100	69.682	
	0.0300	58.971	
	0.2500	35.066	
	0.5000	27.978	
	0.7500	23.055	
	1.0000	19.672	
	1.2500	16.659	
	1.500	14.843	
	1.7500	13.271	
	2.0000	11.9	

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

$$\sigma^2 = \frac{\sum_{i=1}^{n} [\Lambda_i(calcd) - \Lambda_i(obsd)]^2}{n-2}$$

for a sequence of R values and then plotting σ against R; the best-fit R corresponds to the minimum of the σ versus R curve. First, approximate runs over a fairly wide range of *R* values are made to locate the minimum, and then, a fine scan around the minimum is made. Finally, with this minimizing value of *R*, the corresponding Λ° and K_A are calculated.
The values of Λ°, K_A, and R obtained by this procedure for investigated systems are reported in Table 2.

Table 2. Derived conductivity parameters for NaI, NaBr and $NaCH_3COO$ in methanol at 25 °C.

Salt	Λ / (S m^2 ·mol^{-1})	K_A / dm^{-3}·mol^{-1}	R / Å	100σ / Λ°
NaI	107	19.26	10.68	0.009
NaBr	104	67.95	10.44	0.004
$NaCH_3COO$	88	23.00	11.18	0.010
KI	115	17.54	8.23	0.006
KSCN	114	16.29	9.4	0.004
KCH_3COO	96	18.63	10.16	0.007

4. Discussion

The conductance of solutions of KSCN in methanol have also been reported by Barthel et al.[6] The Λ° and K_A of Barthel et al compared with this work.It has been observed that the values of Barthel et al is very near to this study.
The association constants (K_A) indicate that KCH_3COO and KSCN are slightly associated in methanol solutions. The (K_A) values for KCH_3COO and KSCN in methanol solutions decreases by increasing the size of anion.

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NATRİUM VƏ KALİUMUN BƏZİ DUZLARININ METANOL MƏHLULLARININ $25\ ^0C$ TEMPERATURDA ELEKTRİK KEÇİRİCİLİYİ

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Natrium və kalium duzlarının (0.001-1 molyar) konsentrasiyalı məhlullarının $25\ ^0C$ temperaturda elektrik keçiriciliyi təyin edilmişdir. Onzaqerin keçiricilik üçün verilmiş tənliyindən istifadə edərək, məhlulun keçiriciliyi konsentrasiyasının sonsuz azalması halında ekstrapolyasiya üsulu ilə təyin edtlmişdir.

ЭЛЕКТРОПРОВОДНОСТЬ НЕКОТОРЫХ СОЛЕЙ НАТРИЯ И КАЛИЯ В МЕТАНОЛЕ ПРИ $25\ ^0C$

КАРАМАТ НАСИРЗАДЕ, РОГХАИ РАВАШ

Измерены электропроводности некоторых растворов солей натрия и калия концентрацией (0,001-1 моль) при $25\ ^0C$. Значения молярной проводимости при бесконечном разбавлении были получены путем экстраполяции с использованием уравнения проводимости Онзагера. Результаты работы интерпретированы в рамках ион-ионного и ион-растворитель взаимодействий.