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Effect of ethanol on the solvation behaviour of BiI_3 in acetonitrile, methanol and DMF as a function of temperature

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Abstract

This paper reports the results of the investigations carried out on the effect of added ethanol on the conductance behaviour of bismuth tri-iodide in acetonitrile, methanol and dimethylformamide at 288, 298, 308 and 318 K. From the experimental molar conductance value, the limiting molar conductance was determined for all the cases using the Shedlovsky model of conductivity. The limiting molar conductance was found to decrease continuously with the increase in the amount of ethanol either to CH_3CN, CH_3OH or DMF. In pure solvents, conductance varied in the order of $CH_3CN > CH_3OH > DMF > C_2H_5OH$. Association constant was determined in the three solvent systems. Results predicted the endothermic behaviour of the process in most of the cases. Energy of activation of the conducting rate process and thermodynamic parameters of association were calculated and reported. Walden product and corrected Stokes molecular radius were also computed. The solvation number of the species was calculated in the case of pure solvents and the value indicated the existence of solvent shared or separated ion pair in the system.

Keywords: Conductivity; Solvation; Bismuth Iodide; Ion-solvent interaction

1. Introduction

Conductivity measurement is of immense importance in elucidating not only the behaviour of ions in solution but also in the study of solution structural effects and the preferential solvation of ions by a solvent [1,2]. Recently, conductivity studies were made in non-aqueous solvents with the intention of investigating ion–ion and ion–solvent interactions [3,4]. Bismuth exhibits valence +3 state in most of the compounds. Inorganic bismuth salts were the first compounds to be recognized for therapeutic utility [5]. Several groups have used bismuth compounds in various investigations [6–10]. From this laboratory, we have published the conductance behaviour of compounds of bismuth [11] including bismuth tri-iodide (BiI_3) in CH_3OH/CH_3CN+DMF [12]. In continuation of this, we studied the conductivity behaviour of BiI_3 in various solvents, namely acetonitrile (CH_3CN), methanol (CH_3OH), dimethylformamide (DMF), ethanol (C_2H_5OH) and various compositions of acetonitrile+ethanol, methanol+ethanol and DMF+ethanol at (288 K, 298 K, 308 K, 318 K) to elucidate the solvation behaviour of bismuth tri-iodide under prevailing conditions.

2. Materials and methods

Acetonitrile, methanol, dimethylformamide and ethanol were purified as reported [3,12,13]. Commercially available BiI_3 (NR Chem) was used without further purification. Solution of BiI_3 was prepared in ethanol and a known amount of CH_3CN, CH_3OH or DMF was added to it so as to get the required composition of C_2H_5OH. Conductance measurements were made with a standard digital direct reading conductivity meter (CM.180, Elico make, Hyderabad) and a calibrated dip type conductivity cell. The conductivity cell was calibrated [14] by a solution of 0.01 M KCl. Specific conductance of the standard solution was obtained from literature [3] (0.001412

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mho cm^{-1} at 25 °C). It was found to be 0.999 cm^{-1}. All the measurements were made in a thermostat or cryostat maintained at the desired temperature ±0.01 °C.

3. Results and discussion

3.1. Limiting molar conductance

The specific conductance of BiI_3 in various compositions (0%, 20%, 40%, 60%, 80% and 100%) of ethanol (v/v) in $CH_3CN+C_2H_5OH$, $CH_3OH+C_2H_5OH$ and DMF+C_2H_5OH were measured at 288, 298, 308 and 318+−0.01 K. The molar conductance was calculated for all the cases, and the limiting molar conductance (Λ_m^0) was obtained from the following Shedlovsky model of conductivity [15],

$$\frac{1}{S\Lambda_m} = \frac{K_a C \Lambda_m S f_\pm^2}{\Lambda_m^{02}} + \frac{1}{\Lambda_m^0} \tag{1}$$

where

$$S = \left[\frac{\beta\sqrt{C\Lambda_m}}{2\Lambda_m^{o3/2}} + \sqrt{1 + \frac{\beta^2 C\Lambda_m}{4\Lambda_m^{o3}}}\right]^2$$

$$\beta = \frac{8.20 \times 10^5 \Lambda_m^0}{(\in T)^{3/2}} + \frac{82.5}{\eta(\in T)^{1/2}}$$

$$\log f_\pm = \frac{-1.8246 \times 10^6 (C\alpha)^{1/2}/(\in T)^{3/2}}{1 + 50.21 \times 10^8 R(C\alpha)^{1/2}/(\in T)^{1/2}},$$

$$\alpha = S\Lambda_m/\Lambda_m^0 \qquad R = q = e^2/2\varepsilon kT$$

C is molar concentration, ε is dielectric constant, T is absolute temperature, η is viscosity of the solvent, α is degree of dissociation, e is the electronic charge and k is Boltzman constant. The plot of $1/S\Lambda_m$ vs. $C\Lambda_m Sf_\pm^2$ was found to be linear. The initial value of limiting molar conductance required to compute the values of S and β was obtained by applying the theory of Kraus-Bray [16] (Λ_m^0

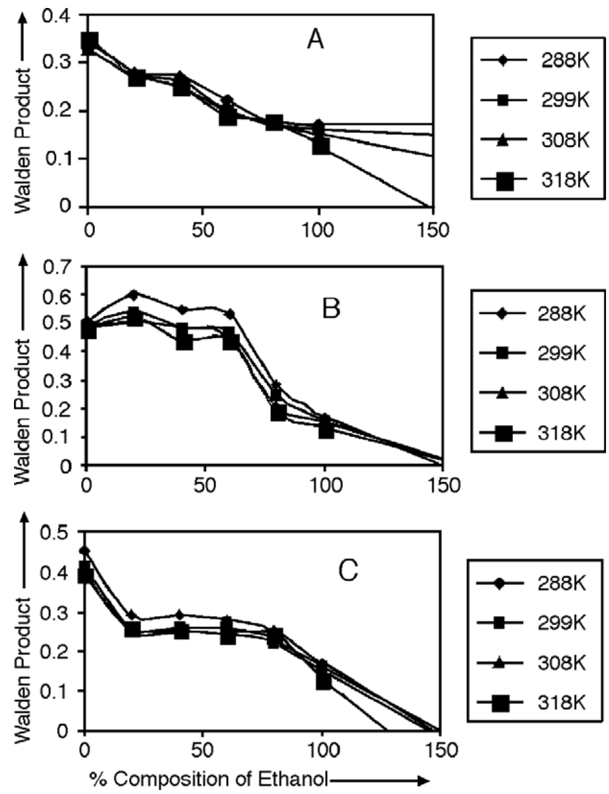

Fig. 1. Plots of Walden product vs. % composition of ethanol for BiI_3 species in (A) $CH_3CN+C_2H_5OH$, (B) $CH_3OH+C_2H_5OH$ (C) DMF+C_2H_5OH.

Table 1
Experimental values of molar conductance at infinite dilution (Λ_m^0: mho cm^2 mol^{-1}) and association constant, K_a for BiI_3 from Shedlovsky model in various solvent compositions (v/v) of $CH_3CN+C_2H_5OH$, $CH_3OH+C_2H_5OH$ and DMF+C_2H_5OH

T (K)	C_2H_5OH (%)											
	0		20		40		60		80		100	
	Λ_m^0	K_a	Λ_m^0	K_a	Λ_m^0	K_a	Λ_m^0	K_a	Λ_m^0	K_a	Λ_m^0	K_a
$CH_3CN+C_2H_5OH$												
288	86.9	17.18	63.2	10.01	57.4	15.54	36.3	47.21	20.4	50.75	13.3	46.60
298	94.3	20.05	69.4	10.71	64.1	16.24	40.0	42.85	23.8	77.74	16.6	58.43
308	102.0	24.02	73.5	11.89	68.4	16.70	43.4	39.36	28.5	124.15	18.5	84.33
318	116.2	30.04	79.3	14.92	74.6	18.36	47.6	32.38	32.7	172.91	20.8	106.80
$CH_3OH+C_2H_5OH$												
288	81.9	17.67	79.3	44.03	60.2	28.55	44.2	35.12	20.0	66.66	13.3	46.60
298	90.9	17.96	86.2	32.05	64.9	30.52	51.5	39.48	22.2	55.54	16.6	58.43
308	100.0	18.93	94.3	21.90	74.6	33.83	57.4	46.62	23.8	50.35	18.5	84.33
318	113.6	22.26	107.5	35.12	78.1	23.12	66.6	53.50	25.0	26.78	20.8	106.80
DMF+C_2H_5OH												
288	51.5	10.73	31.2	12.20	30.7	14.97	28.1	14.86	22.7	33.66	13.3	46.60
298	56.1	9.85	33.8	7.83	32.7	11.31	31.2	18.60	25.6	22.78	16.6	58.43
308	61.7	8.06	37.0	6.23	35.7	10.63	33.3	14.48	27.7	21.42	18.5	84.33
318	66.6	7.56	41.6	7.23	39.2	8.54	36.3	9.44	32.7	23.87	20.8	106.80