

Ionic Conductivity in Binary Solvent Mixtures. 3. Dimethyl Sulfoxide + Propylene Carbonate at 25 °C

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Electrolytic conductance measurements for potassium alkyl xanthates (alkyl: methyl, ethyl, 2-propyl, butyl, and 3-methyl-1-butyl) are reported at $x_A = 0.20, 0.40, 0.60, 0.80$ dimethyl sulfoxide (A) + propylene carbonate (B) mixtures at 25 °C. The results are analyzed by the Fuoss conductance–concentration equation. Values of limiting molar conductance Λ_0 , association constant K_A , and cosphere diameter R are obtained, and an attempt is made to relate these parameters to the increasing size of the attached alkyl substituents in the xanthate anion.

1. Introduction

Binary solvent mixtures have been receiving increasing attention in analytical determinations and as nonaqueous battery solvents. Studies on ionic conductivity of certain ions in propylene carbonate + ethylene carbonate (Srivastava and Samant, 1994) and ethylene carbonate + water mixtures (Srivastava et al., 1996) have been reported in our previous work.

Propylene carbonate (4-methyl-1,3-dioxolane-2-one, or PC) is a stable dipolar aprotic solvent ($t_m = -49.2$ °C, $t_b = 241.7$ °C) of a moderately high relative permittivity (64.4 at 25 °C), and it dissolves a variety of organic and inorganic substances. Studies have indicated that the negative end of the dipole is localized on carbonyl oxygen whereas the positive charge is distributed over the atoms in the chain $H_3C-CH-CH_2-$ (Mukherjee, 1975), and thus, cations are more solvated than anions in PC.

Dimethyl sulfoxide (DMSO) is a dipolar aprotic solvent. It has a broad convenient liquid range ($t_m = 18$ °C, $t_b = 189$ °C), an intermediate relative permittivity (46.68 at 25 °C), and extensive dissolving power. DMSO has been selected for the present study as it has similar properties to PC. It has a negative center located at the oxygen atom (Maxey and Popov, 1967). The donor numbers of DMSO and PC are 29.8 (Coetzee, 1976) and 15.1 (Reichart, 1979), respectively, which indicate that DMSO is more basic than PC. Properties of DMSO + PC mixtures enable them to behave like good solvents in which ion–dipole type solute–solvent interactions are favored.

The conductance studies on potassium alkyl xanthates in PC (Srivastava et al., 1988) and DMSO (Srivastava and Jagasia, 1995) have already been reported. The purpose of this work was to study the behavior of potassium alkyl xanthates possessing symmetrically large ions (alkyl: methyl, ethyl, 2-propyl, butyl, 3-methyl-1-butyl) in dimethyl sulfoxide + propylene carbonate mixtures conductometrically, to determine their ionic mobilities, and to correlate the observed behavior with the solvent properties.

2. Experimental Section

2.1. Chemicals. 2.1.1. Solvents. Commercially available DMSO (99% pure; SISCO, India) was held over sodium

Table 1. Relative Permittivity ϵ , Density ρ , and Viscosity η for DMSO (A) + PC (B) Mixtures at 25 °C^a

x_A	ϵ	$\rho/g\text{ cm}^{-3}$	$\eta/\text{mPa s}$
0.0	64.7	1.199	2.50
0.2	62.0	1.178	2.27
0.4	59.1	1.157	2.11
0.6	55.7	1.136	2.02
0.8	51.8	1.115	1.96
1.0	46.9	1.095	1.98

^a Lee, 1976.

hydroxide for 3 h at 90 °C and distilled twice at reduced pressure. Finally a third distillation was carried out without any additive, under reduced pressure. The middle fraction, comprising about 80%, was collected and used in the present investigation. The specific conductance of the purified solvent ranged between 3×10^{-8} and 4×10^{-8} S cm^{-1} at 25 °C.

Initially, *p*-toluenesulfonic acid (2 g dm^{-3}) was added to PC (99% pure; Fluka) and was shaken well to remove any basic impurities. The supernatant liquid was stored over dried 0.5 nm molecular sieves (10 g dm^{-3}) for a prolonged period of time with intermittent stirring, and then two successive distillations were carried out under reduced pressure in the presence of the molecular sieves. A third distillation was carried out without any additive. The middle fraction boiling at 80 °C and a pressure of 133.32 Pa was used in the present investigation. The specific conductivity of the purified solvent varied from (2×10^{-8} to 3×10^{-8}) S cm^{-1} at 25 °C.

Gas chromatographic analysis of the purified solvents did not reveal the presence of any organic impurities and water.

Both the solvents were stored in sealed containers to prevent contamination from CO₂ and water.

Known masses of DMSO and PC were mixed together to obtain desired compositions prior to use with an accuracy of ± 0.001 mole fraction (mf). All solutions were prepared using a single-pan balance (K. Roy, India) with ± 0.01 mg precision.

2.1.2. Reagents. Potassium alkyl xanthates were prepared by the reaction of alkyl alcohols, carbon disulfide, and potassium hydroxide following known literature methods (Rao, 1971; Reid, 1962; Vogel, 1971). The products were later recrystallized with absolute alcohol. Purity of

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Table 2. Molar Conductance Λ at Concentration c of Various Xanthates in DMSO (A) + PC (B) Mixtures at 25 °C

$x_A = 0.2$		$x_A = 0.4$		$x_A = 0.6$		$x_A = 0.8$	
$10^4 c / \text{mol dm}^{-3}$	$\Lambda / \text{S cm}^2 \text{ mol}^{-1}$	$10^4 c / \text{mol dm}^{-3}$	$\Lambda / \text{S cm}^2 \text{ mol}^{-1}$	$10^4 c / \text{mol dm}^{-3}$	$\Lambda / \text{S cm}^2 \text{ mol}^{-1}$	$10^4 c / \text{mol dm}^{-3}$	$\Lambda / \text{S cm}^2 \text{ mol}^{-1}$
Potassium Methyl Xanthate							
195.6	22.31	227.8	24.91	169.1	27.33	233.2	28.21
146.7	22.99	207.3	25.20	127.6	27.92	199.4	28.52
117.2	23.58	180.9	25.50	111.6	28.25	160.1	29.15
81.3	24.54	144.0	26.20	93.2	28.35	136.2	29.57
68.7	24.79	119.2	26.71	88.5	28.61	116.5	29.98
48.4	25.40	80.4	27.42	71.7	28.97	108.6	30.09
37.8	25.87	44.2	28.28	59.7	29.35	97.4	30.35
30.1	26.22	24.0	29.00	32.8	29.72	76.3	30.91
20.5	26.77			17.8	30.41	46.2	31.68
Potassium Ethyl Xanthate							
231.4	21.67	210.0	22.84	178.3	25.47	232.3	25.41
211.2	21.95	173.8	23.41	164.9	25.48	188.0	26.12
193.2	22.20	135.5	24.00	150.8	25.82	161.2	26.51
169.5	22.56	126.7	24.22	141.6	25.86	130.0	27.06
144.0	23.00	97.5	24.90	115.4	26.46	94.0	27.89
115.0	23.45	84.5	25.19	93.6	26.95	77.8	28.31
80.8	24.02	55.7	25.88	78.9	27.42	60.4	28.80
48.9	24.93	39.7	26.58	68.2	27.48	41.7	29.40
31.2	25.58	22.4	27.34	56.9	27.84	21.7	30.20
Potassium 2-Propyl Xanthate							
162.2	20.23	166.4	22.49	155.4	23.30	158.1	25.84
128.0	20.89	137.5	22.99	130.5	23.84	142.6	26.03
107.0	21.15	120.1	23.33	112.1	24.20	124.7	26.24
82.7	21.73	100.1	23.70	71.2	25.15	107.2	26.75
67.2	22.10	76.8	24.10	49.0	25.82	104.2	26.72
54.2	22.50	49.6	24.69	30.1	26.44	80.4	27.30
38.4	22.98	24.1	25.39	28.5	26.47	52.4	27.99
27.6	23.37	9.8	26.29	9.1	27.52	36.0	28.4
12.7	24.19	7.6	26.38			26.3	28.75
11.2	24.33						
Potassium Butyl Xanthate							
222.0	19.37	194.5	21.19	175.8	23.33	156.9	24.24
189.3	19.99	140.8	21.96	141.2	23.69	141.6	24.45
174.4	20.09	117.5	22.38	95.7	24.49	129.9	24.66
156.2	20.40	90.6	22.84	81.0	24.80	113.6	24.94
138.5	20.68	72.4	23.32	67.2	24.97	94.9	25.33
108.1	21.20	43.8	24.12	40.7	25.68	73.2	25.78
91.2	21.63	29.5	24.58	26.0	26.14	47.7	26.50
72.2	21.90	12.9	25.40				
61.5	22.22						
Potassium 3-Methyl-1-butyl Xanthate							
144.0	19.90	189.0	20.58	146.5	22.62	202.5	23.88
128.4	20.21	150.0	21.18	130.3	22.88	187.2	24.08
102.0	20.70	98.8	22.25	111.9	23.26	150.3	24.60
84.6	20.95	66.7	22.76	90.7	23.75	121.0	25.00
72.2	21.35	48.8	23.33	81.2	23.83	101.9	25.39
57.0	21.68	36.7	23.75	65.9	24.24	71.6	25.90
37.2	22.35	24.5	24.24	54.8	24.50	43.4	26.70
31.3	22.50			30.1	25.20		
				9.1	26.18		

the xanthates was determined using acid–base titration methods and was found to be >99% in each case.

All other chemicals used were of analytical reagent grade.

2.2. Conductance Measurements. All conductance values were measured at (25 ± 0.05) °C using a dip type cell constant (1.080 ± 0.001) cm^{-1} with lightly platinized electrodes. The working solutions were prepared by adding an aliquot of stock solution to a known volume of solvent. After each addition of the stock solution, it was mixed well and allowed to attain the temperature of the air bath. A Toshniwal digital conductivity meter type CLO 1.10 A (200 Hz; 3 kHz) was used in the measurement. The conductivity meter was standardized regularly using standard KCl solutions. The reported conductivities refer to a frequency of 200 Hz; no significant variation in conductivities was noticed on using the other frequency. Experiments were repeated at least twice for concordant results to give reproducibility in Λ_0 values within ± 0.1 $\text{S cm}^2 \text{ mol}^{-1}$. All

molar conductivities reported have been calculated after the correction for the solvent conductivity.

3. Results and Discussions

The results of conductivity measurements were analyzed by the Fuoss (1978) conductance–concentration equation (Fuoss, 1978), which is based on the model of coupled-equilibria



where the symbol $(\text{A}^+ \cdots \text{B}^-)$ represents a solvent separated pair, $\text{A}^+ \text{B}^-$ a contact pair, and AB a neutral molecule. For a given set of conductivity values (C_j , Λ_j ; where $j = 1, \dots, n$), preferably spanning a concentration range of at least a decade, the three adjustable parameters, the limiting molar conductivity Λ_0 , the association constant K_A , and cosphere

Table 3. Derived Conductance Parameters in DMSO + PC Mixtures at 25 °C

x_A	$\Lambda_0 \pm \Delta\Lambda_0/S \text{ cm}^2 \text{ mol}^{-1}$	K_A	$R/\text{\AA}$	$100\sigma/\Lambda_0$
Potassium Methyl Xanthate				
0.2	28.31 ± 0.05	51.94	17.3	0.19
0.4	29.99 ± 0.12	14.95	6.0	0.59
0.6	31.34 ± 0.10	13.21	5.8	0.34
0.8	34.07 ± 0.04	17.75	6.7	0.08
Potassium Ethyl Xanthate				
0.2	27.07 ± 0.07	26.13	11.0	0.23
0.4	28.85 ± 0.06	37.86	14.0	0.19
0.6	30.11 ± 0.14	27.98	15.2	0.30
0.8	31.71 ± 0.02	20.53	6.4	0.08
Potassium 2-Propyl Xanthate				
0.2	25.19 ± 0.04	54.02	17.8	0.20
0.4	26.92 ± 0.07	41.38	16.4	0.10
0.6	28.21 ± 0.04	19.03	2.9	0.17
0.8	30.26 ± 0.06	18.45	6.8	0.20
Potassium Butyl Xanthate				
0.2	24.60 ± 0.11	19.50	4.7	0.28
0.4	26.12 ± 0.03	43.98	18.9	0.14
0.6	27.38 ± 0.04	15.89	5.5	0.15
0.8	28.84 ± 0.03	36.85	14.3	0.05
Potassium 3-Methyl-1-butyl Xanthate				
0.2	24.15 ± 0.06	36.84	13.7	0.18
0.4	25.54 ± 0.08	26.21	9.5	0.31
0.6	26.80 ± 0.04	17.50	3.8	0.19
0.8	28.62 ± 0.06	26.84	11.7	0.13
Potassium Perchlorate				
0.0	29.65 ± 0.05	61.39	21.8	0.16
0.2	31.22 ± 0.06	57.20	22.4	0.31
0.4	33.32 ± 0.06	11.48	5.4	0.19
0.6	35.01 ± 0.05	15.86	6.3	0.15
0.8	37.16 ± 0.06	40.04	18.9	0.13
1.0	38.89 ± 0.07	22.32	7.3	0.16

diameter R are derived from the following equations

$$\Lambda = p[\Lambda_0(1 + \Delta X/X) + \Delta\Lambda_e]$$

where

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

and

$$\gamma = 1 - K_A c \gamma^2 f^2$$

$$\ln f = -\beta\kappa/2[1 + \kappa R]$$

where Λ denotes molar conductance, p is the fraction of the solute that contributes to the conductance current, α denotes the fraction of paired ions present as contact pairs, γ denotes the fraction of solute present as unpaired ions, f is the activity coefficient, and $\Delta X/X$ and $\Delta\Lambda_e$ are the relaxation and electrophoretic terms respectively, which are functions of C_j , R , and ϵ . Other notations used in these equations are the same as those used by Fuoss (Fuoss, 1978). The program "SCAN ON RHO" was used to compute the conductance parameters.

To accomplish the required calculations, input for the program is the data set (C_j , Λ_j), the relative permittivity ϵ , viscosity η , estimated values for α and Λ_0 and instructions to cover a preselected range of R values. The physical properties of DMSO + PC mixtures are given in Table 1 (Lee, 1976). On the basis of the relative permittivity of the solvent, the initial α is set at 0.75 and initial value of Λ_0 is obtained from a freehand extrapolation of the Kohlrausch plot. The molar conductance values Λ as a function of concentration c in the four compositions of DMSO + PC mixture, at 25 °C, are given in Table 2. The best fit conductance parameters and the

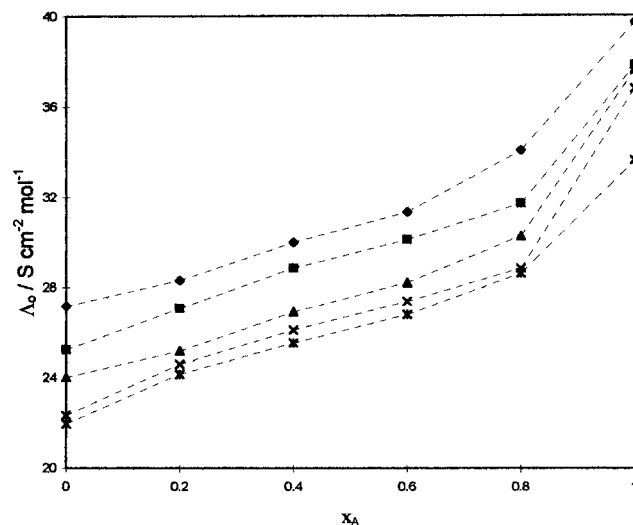


Figure 1. Variation in limiting molar conductance of various potassium alkyl xanthates with x_A : KMX (◆); KEX (■); KPX (▲); KBX (×); KMBX (*).

Table 4. Limiting Ionic Conductivity of Cations and Anions in DMSO + PC Mixtures at 25 °C

$\lambda/S \text{ cm}^2 \text{ mol}^{-1}$	x_A					
	0.0 ^a	0.2	0.4	0.6	0.8	1.0 ^b
K^+ ^c	9.70	10.70	11.60	12.80	13.60	14.40
MX^-	17.48	17.61	18.39	18.54	20.47	25.31
EX^-	15.54	16.37	17.25	17.31	18.11	23.39
PX^-	14.32	14.49	15.32	15.41	16.66	23.21
BX^-	12.64	13.90	14.52	14.58	15.24	22.37
MBX^-	12.27	13.45	13.94	14.00	15.02	19.21

^a Srivastava et al., 1988. ^b Srivastava and Jagasia, 1995. ^c Wawrzyniak, 1991.

other constants derived from analysis of conductance data corresponding to the minimum in the $\sigma\% - R$ curve, where $\sigma\%$ is the standard deviation, are presented in Table 3.

As evident from Table 3, a decrease in the limiting molar conductance Λ_0 is observed with increasing size of the xanthates from potassium methyl to potassium 3-methyl-1-butyl xanthates. The limiting molar conductance for each of the systems shows an increase from the PC-rich region to the DMSO-rich region (Figure 1), which could well be attributed to a decrease in the viscosity of the solvent system toward the DMSO-rich region and preferential solvation of ions in the PC-rich region.

Table 4 contains estimates of the limiting anionic conductivities (λ^\ominus) for each system in these solvent systems assuming negligible association at infinite dilution. The limiting ionic conductance λ^\ominus , for xanthate ions was calculated by subtracting the values of $\lambda_{K^+}^\ominus$ (Wawrzyniak, 1991) from the experimentally obtained Λ_0 value of various potassium alkyl xanthates. The literature value for $\lambda_{K^+}^\ominus$ was further confirmed by performing conductance experiments for $KClO_4$ in all the above solvent systems including pure DMSO and PC recorded in Table 3. $\Lambda_{KClO_4}^\ominus$ so obtained was in agreement with the values of $\lambda_{K^+}^\ominus$ and $\lambda_{ClO_4^-}^\ominus$ given in the literature (Wawrzyniak, 1991).

The variation of the salt and ionic Walden products for each system with varying mole fraction of DMSO are presented in Figures 2 and 3. They follow the same pattern. Initial decrease in $\Lambda_0\eta$ values from $x_A = 0.0$ to 0.2, almost remaining constant from $x_A = 0.2$ to 0.6 and an increase from $x_A = 0.6$ to 1.0 have been observed.

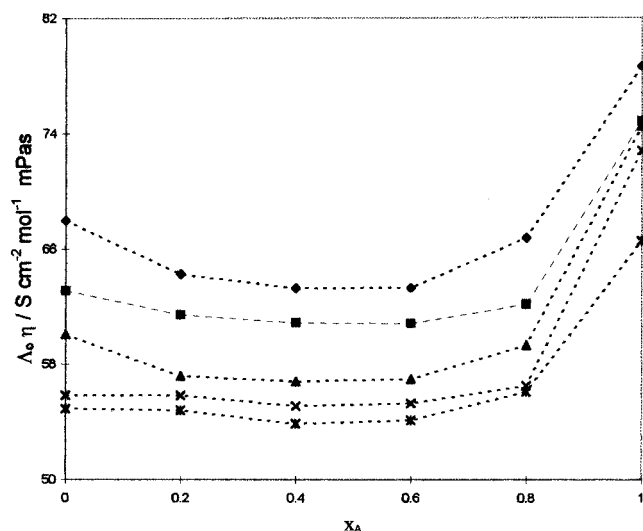


Figure 2. Variation in Walden product of various potassium alkyl xanthates with x_A : KMX (◆); KEX (■); KPX (▲); KBX (×); KMBX (*).

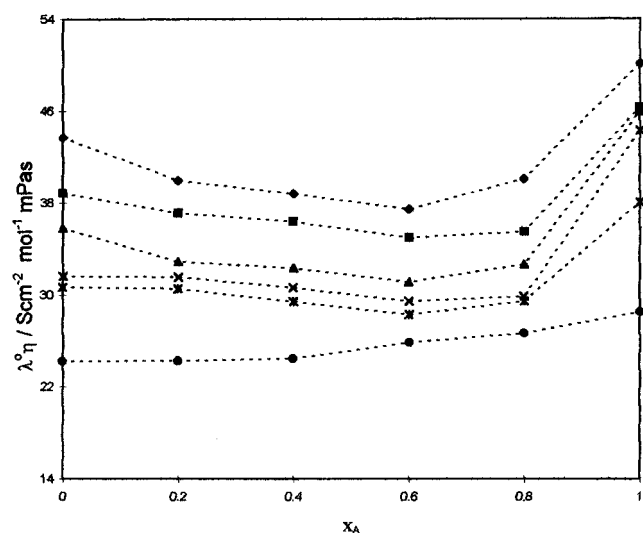


Figure 3. Variation in ionic Walden product of various xanthates and potassium with x_A : MX^- (◆); EX^- (■); PX^- (▲); BX^- (×); MBX^- (*); K^+ (●).

The Walden product, being a product of limiting molar conductivity and viscosity, is observed to be high for $x_A = 0.0$ as the viscosity of the solvent system is more. An abrupt decrease in the viscosity in the solvent at $x_A = 0.2$ explains the sudden decrease in the Walden product from $x_A = 0.0$ to 0.2 , thereafter remaining constant from $x_A = 0.2$ to $x_A = 0.6$. Further increase in the Walden product from $x_A = 0.6$ to $x_A = 1.0$ could be well attributed to less solvation of electrolytes in DMSO as compared to PC and PC + DMSO mixtures.

The association constant or conductometric pairing constant K_A for all the systems given in Table 3 are found to be generally appreciable for $K_A > 10$, which reflects some sort of significant association in these solvent mixtures. An attempt was made to correlate the conventional $\log K_A$ vs $1/\epsilon$ plots, but these showed no linear variation for the salts

studied. This indicates that ion association may not be solely dependent on the dielectric constant of the medium; however, other factors such as shape, size, dipole moment, polarizability, and possibly other details of solvent/solute interactions could also be taken into account for the rationalization of the K_A values obtained in the present work.

The cosphere diameter (R) values for all the xanthates under study in DMSO + PC mixtures are given in Table 3. As R is the measure of the extent of influence of the ionic charge in the solvent and consequently the ionic association, R values are expected to increase with decrease in the dielectric constant of the solvents, but no significant trend has been observed. Since the best fit conductance parameters are reproduced equally well over a wide range of arbitrarily chosen R values, a comprehensive correlation of the cosphere diameter of the respective systems could not be made; the same has also been noticed by Fuoss and several other workers (Fuoss, 1978; Bahadur and Ramamurti, 1980; Shiavo et al., 1979).

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