

CHAPTER VIII

Electrical Conductance of Alkali Chlorides in Mixed Solvents: Methanol + Carbon Tetrachloride and Methanol + 1,4-Dioxane at 298.15 K*

8.1. *Introduction*

Study of electrical conductance of mixed organic solvent systems plays a significant role in examining the nature and magnitude of ion-ion and ion-solvent interactions.¹⁻⁷ Other solvent properties such as viscosity and permittivity have also been taken into account in determining the extent of these interactions.

1, 4-dioxane is a good industrial solvent and figures prominently in the high-energy battery technology⁸ and has also found its application in the organic syntheses.^{9,10,11,12} Carbon tetrachloride is used to make compounds such as Chlorofluoromethanes, used as refrigerants and aerosol-spray propellants, in fire extinguishers and for dry cleaning of fabrics. Methanol is very widely used in industry, including the manufacture of pharmaceuticals and cosmetic products, in enology and as an energy source.¹³

The alkali metal salts, specially, Li salts has been used for many years in non-aqueous batteries.⁸ In such systems, the choice of electrolyte solution and optimization of its salt concentration are two important factors. An electrolyte possessing high specific conductivity and, hence, minimal ion-ion interaction is required to maintain the cell at low resistance. Knowledge of the application of the solvent and solute studied and the state of association of the electrolytes and their interactions with solvent molecules is essential for the optimal choice of solvent and electrolyte¹⁴.

Methanol is extremely self-associated by hydrogen bonding in pure state¹⁵. But, this type of strong intermolecular forces are either very weak or totally absent in case of carbon tetrachloride or 1,4-dioxane while the dipole-induced dipole forces along with dispersive forces predominate in these cases.

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The conductance and viscosity of three alkali chlorides is studied to reveal the nature of ionic association and mobility of ions in these mixed solvent systems, which have not been studied earlier as per available literature.

In the present work, an attempt has been made to ascertain the complete nature of ion-solvent, solvent-solvent interactions of the alkali metal chlorides in solvent mixtures of methanol with carbon tetrachloride and 1,4-dioxane at 298.15 K. A comparison between the natures of interactive forces operating in these two different solvent systems is also analyzed.

8.2 Experimental Section

8.2.1. Materials

Lithium chloride (Merck, India), Sodium chloride (Loba Chemie) and Potassium chloride (Merck, India) was recrystallized, dried by the procedures mentioned in Chap III and stored in desiccators before use.

Methanol (Merck, India, Uvasol grade, 99.5% pure) was dried over 3Å molecular sieves and distilled fractionally. Carbon tetrachloride (Merck, India) was dried, and distilled as mentioned procedures (vide Chap III). 1,4-dioxane (Merck, India) with initial water content of 120 ppm found by Karl-Fischer titration and 0.15% impurities found by gas chromatography was used after redistillation¹⁰.

The purity of the solvents was ascertained by GLC and also by comparing experimental values of densities and viscosities with those reported in the literature as listed in Table 1.

8.2.2. Apparatus and Procedure

Digital Temperature controller BP-41 (Bose-Panda Instruments, India) (± 0.1 K) was used to maintain the temperature.

Conductance measurements of the solvent systems were executed in a Systronic 308 conductivity-TDS meter (accuracy $\pm 0.1\%$) working at a frequency of 1kHz, using a dip type immersion cell (cell constant 1.07at 298.15 K).

Densities (ρ) were measured at the mentioned temperatures with an Ostwald-Sprengel type pycnometer having bulb volume of about 25 cm³ and an internal diameter of the capillary of about 1 mm. Viscosities (η) have been measured by means of a suspended Ubbelohde type viscometer³¹. The details of density and viscosity

measurements were described earlier^{9, 23} in Chap III. The precision of the density and viscosity measurements is $\pm 3 \times 10^{-4} \text{ g.cm}^{-1}$ and $\pm 2 \times 10^{-4} \text{ m.Pa.s}$ respectively.

All the solvent mixtures were prepared by mass. Three sets of each binary solvent mixtures (90.6%, 82.31%, 66.89%) of methanol with carbon tetrachloride and 1,4-dioxane having mole fractions of methanol (x_1) as 1.0000, 0.97885, 0.95712, 0.90657 and 1.0000, 0.96364, 0.92747, 0.84752 respectively were chosen as the solvent media for present study. A stock solution of each salt was prepared by mass and working solutions were prepared by weight dilution.

8.3. Results and Discussion

The physical properties of the pure solvent and solvent mixtures are given in Table 1, where ϵ is the dielectric constant, ρ_0 is the density (Kg.m^{-3}) and η_0 is the viscosity (m.Pa.s). Conductivities of electrolyte solutions as a function of molar concentration (c) are given in Table 2 in different solvent mixtures at 298.15K.

Permittivity (ϵ) of the solvent-mixtures were estimated by a computerized extrapolation programme, using ϵ and $W\%$ values from literature¹⁴. The conductance data have been analyzed by Fuoss conductance- concentration equation. (Fuoss, 1978 a, b).^{16,17}

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

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

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

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

$$\beta = \frac{e^2}{\epsilon k T} \quad (5)$$

$$K_A = \frac{K_R}{(1 - \alpha)} = K_R(1 + K_S) \quad (6)$$

Where, R_x is the relaxation field effect, E_L is the electrophoretic counter current, κ^{-1} is the radius of the ion atmosphere, ϵ is the relative permittivity of the solvent, e is the electron charge, k is the Boltzmann constant, γ is the fraction of solute present as unpaired ion, f is the activity coefficient, c is the molarity of the solution, T is the absolute temperature, β is twice the Bjerrum distance, and α denotes the fraction of the paired ions, K_R describes the formation and separation of

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solvent separated pairs by diffusion in and out of spheres of diameter R around cations, and K_S is a constant describing the short range process by which contact pairs form and dissociate. K_R and K_S are given as follows,

$$K_R = \frac{(1-\alpha)(1-\gamma)}{c\gamma^2 f^2} \quad (7)$$

$$K_S = \frac{\alpha}{(1-\alpha)} \quad (8)$$

The computations were performed in a computer using the programme suggested by Fuoss. The initial Λ_0 values for iteration procedure were obtained from Shedlovsky extrapolation¹⁹ of the data. Input for the program is the set,

$$(C_j, \Lambda_j, j = 1, \dots, n), n, \eta, \epsilon, T,$$

initial value of Λ_0 and a set of instructions to cover a protected range of R values.

In practice calculations were performed by fitting the values of Λ_0 and σ , which minimize the standard deviation (σ),

$$\sigma^2 = \sum \left[\frac{(\Lambda_{jcalc} - \Lambda_{jobs})^2}{(n-2)} \right] \quad (9)$$

For a sequence of R values and then plotting σ against the best-fit R corresponds the minimum of σ versus R curve. First, approximate run over a fairly wide range of R values are made to locate the minimum and then a fine scan around the minimum was made. Finally with this minimizing value of R , corresponding Λ_0 and K_A were calculated.

In the present analysis, however, since a rough scan of R values gave no significant minima in the (σ % vs. R) curves, the R value was assumed to be, $R = a + d$ where, a is the sum of crystallographic radii and d , the average distance corresponding to the side of a cell occupied by a solvent molecule. The distance ' d ' is given by,¹⁷

$$d(A^0) = 1.183 \left(\frac{M}{\rho_0} \right)^{\frac{1}{3}} \quad (10)$$

Where, M is the molar weight of the solvent and ρ_0 is its density. In mixed solvent studies M is replaced by the mole fraction average molecular weight M_{AV} , given by,

$$M_{AV} = \frac{M_1 M_2}{(W_1 M_2 + W_2 M_1)} \quad (1)$$

Where, W_1, W_2 and M_1, M_2 are the weight fraction and molecular weight of the first and second component respectively. Though, this is an over simplification ignoring possible selective solvation, it at least provides a self consistent way to obtain an acceptable value for the parameter when a broad range of R values fits the data.

The limiting equivalent conductance, (Λ_0), the association constant (K_A), and the Walden products ($\Lambda_0 \eta_0$) for the three salts at all the mole fractions of the solvent mixtures studied here are recorded in Table 3. These data are interpreted in terms of ion-solvent and ion-ion interactions and structural changes in the mixed solvent systems.

It is observed from Table 3 that, the limiting equivalent conductance Λ_0 values for alkali chlorides increases with the increase in size of the cation for any mole fraction of the mixed solvent systems. For the three alkali chlorides, having common anion, the Λ_0 value is enhanced by the following order:



The trend of variation of Λ_0 values predicts the relative actual sizes of these ions as they exist in solution.¹⁸ Thus the actual sizes of the cations as they exist in solution, follow the order:

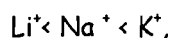


This is due to solvation of the ions by the solvent mixtures. For these electrolytes having the common anion, as the size of the cation increases, the solvation decreases. So, it can be said that, Li^+ , which has the largest size in solution, is the most solvated one, and K^+ , having the smallest size is the least solvated one.¹⁹

The conductivity enhancement in case of solvent mixtures can qualitatively be well explained by a favorable combination of high permittivity and low viscosity of solvents as observed by some researchers²⁰. In the discussed solvent mixtures, methanol is the common solvent having higher permittivity compared to 1,4-Dioxane or Carbon tetrachloride. In both the solvent mixtures the conductivity measurements were done by taking the same salts. So, the combination of a solvent of higher permittivity (Methanol) with the one having low viscosity of (1,4-Dioxane) has comparatively higher mobility resulting in higher conductivity values.

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The associations constant (K_A), as recorded in Table 3 indicates that, all the salts are highly associated in both the solvent mixtures. This is expected because of the lower permittivity of the components added.²¹ For the alkali metal chlorides studied here, the K_A values decreases with increasing size of the cations in the order:



This is due to an apparent decrease in ion dipole interactions.^{5,22,23}

It is further seen from Table 3 that Λ_0 values decrease gradually with the addition of CCl_4 or 1,4 Dioxane to pure methanol with corresponding increase in K_A values. This indicates that association of ions increase with the addition of 1,4-dioxane or CCl_4 to pure methanol rendering to the decrease of the mobility of ions in the mixture and thereby decreasing Λ_0 values. The significantly large values of K_A and exothermic ion-pair formation in the solvent mixture indicate the presence of specific short-range interaction within the ion-pair.

The values of Walden product ($\Lambda_0\eta_0$) for the studied electrolytes pass through a maximum at about 0.97885 mole fraction of methanol, in methanol carbon tetrachloride solvent system, whereas for, methanol, 1,4-dioxane solvent system, the Walden product is maximum at 0.96364 mole fraction of methanol (table 3). The Walden products then decrease continuously for all the lower mole fractions. The representative plots for the selected chlorides for solvent mixture 1, (methanol+ carbon tetrachloride) is given in figure 1, and that for solvent mixture 2, (methanol + 1,4- dioxane) is given figure 2.

There are lots of models to account for the dependence of the Walden product on solvent composition. The theory based on "gel effect,"^{24,25} proposes that, the initial increment in $\Lambda_0\eta_0$ is due to migration process, occurring free of viscous force through the interstices created by long range order in the solvent. Some researchers²⁶ have also put forward a 'sorting mechanism' depending upon the 'acid base properties' of the organic solvent. It is suggested that, in this experiment, ion- methanol interactions are stronger than ion- carbon tetrachloride or ion- 1,4-dioxane interactions presumably because of the weaker acid- base properties of the later two solvent components. The theory envisages a comparative enrichment of methanol in the ionic co sphere and this causes the local viscosity near the ions to be lower than the bulk viscosity of the solvent

medium, which in turn increases the mobility and as a result the Walden product appears higher for the next solvent mixtures. The theories based on solvent- dipole relaxation effects ^{27,28} can be used to explain the decrease in Walden product ($\Lambda_0\eta_0$) as the carbon tetrachloride or 1,4-dioxane concentration in the solvent mixture increases. It is generally accepted that, retardation due to relaxation of solvent dipoles around the ions in motion can decrease their mobility and the dielectric-shifting coefficient can be computed. However, to obtain meaningful data, it is essential to take into account the microscopic nature of the solvent in the vicinity of the ions as also the influence of the ions in the structure of the solvent.

There is another proposed scheme based on the assumption that, the progressive addition of carbon tetrachloride or 1,4-dioxane to methanol causes initial contraction of the solvation sheath around the ions present in solvent media. This "desolvation effect" ^{24,29} decreases the effective size of the cations and anions and as a result, the ionic mobility and Walden product of the salts can increase initially in the methanol rich region of the mixture. Gluekuf, ³⁰ has noted that, as the ion size decreases, its first solvation sheath also contracts and therefore the friction between this layer and the ion increases. It appears that, this enhanced drag of the solvation layer decreases the mobility and so the Walden product ($\Lambda_0\eta_0$) shows a maximum at a particular solvent composition and then decreases monotonously. Extensive solvation of the ions with carbon tetrachloride or 1,4-dioxane can also decrease the mobility of the ions but this process is significant at higher concentration of carbon tetrachloride or 1,4-dioxane in the solvent mixture and helps in the continuous decrease of Walden product ($\Lambda_0\eta_0$).

It should still be mentioned²⁵ that, the theories discussed here or other contemporary theories do not predict quantitatively either the value of the maximum or its enhanced dependence for certain electrolytes in different solvent medium.

8.4 Conclusion:

In this chapter, the conductance and viscosity of three alkali chlorides is studied to reveal the nature of ionic association and mobility of ions in methanol+ carbon tetrachloride and methanol + 1,4- dioxane mixed solvent systems. It is found that, for these electrolytes having the common anion, as the size of the cation increases, the

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solvation decreases. All the salts are highly associated in both the solvent mixtures. Also the combination of a solvent of higher permittivity with the one having low viscosity of has comparatively higher mobility resulting in higher conductivity values. The values of Walden product for the studied electrolytes pass through a maximum at a particular mole fraction and then decrease continuously for all the lower mole fractions. These are the main conclusions drawn from the above conductance study.

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Table 1.
Physical Properties of solvent Mixtures at 298.15 K.

Methanol + Carbon tetrachloride				
Mass% of Methanol	x_1	ϵ	$\rho_0 \times 10^{-3}$ /Kg .m ⁻³	η_0 / mPa.s
100.00	1	32.66	0.7866	0.5470
90.60	0.97885	26.72	1.0313	0.5672
82.31	0.95712	22.22	1.0401	0.5875
66.89	0.90657	15.31	1.0405	0.6438
Methanol + 1,4-Dioxane				
100.00	1	32.66	0.7866	0.5470
90.60	0.96364	29.12	0.8058	0.5589
82.31	0.92747	26.41	0.8225	0.5488
66.89	0.84752	21.25	0.8570	0.5684

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Table 2.

Electrical conductance Λ as a function of concentration c for alkali chlorides in mixed solvents at 298.15 K.

$c \times 10^4$	Λ	$c \times 10^4$	Λ	$c \times 10^4$	Λ
/mol.dm ⁻³	/S.cm ³ mol ⁻¹	/mol.dm ⁻³	/S.cm ³ mol ⁻¹	/mol.dm ⁻³	/S.cm ³ mol ⁻¹
Methanol + Carbon tetrachloride					
$x_1 = 1.0000$					
LiCl		NaCl		KCl	
12.35,	83.2	12.54,	89.1	13.53,	94.2
21.17,	76.8	21.49,	83.3	23.20,	87.7
27.79,	72.6	28.21,	79.4	30.45,	84.5
32.94,	69.2	33.43,	76.6	36.09,	81.4
37.06,	67.5	37.61,	74.3	40.06,	79.4
40.43,	65.8	41.03,	73.1	44.29,	78.2
43.24,	64.9	43.88,	71.8	47.37,	77.2
45.62,	63.6	46.29,	70.6	49.97,	75.6
47.66,	62.6	48.36,	69.6	52.20,	74.9
49.42,	62.4	50.15,	68.7	54.13,	74.6
50.96,	61.8	51.72,	67.7	55.82,	74.1
52.32,	60.9	53.10,	67.1	57.31,	73.5
$x_1 = 0.97885$					
6.37,	82.7	7.76,	86.8	7.74,	92.3
10.92,	76.6	13.30,	80.3	13.26,	85.5
14.33,	72.9	17.46,	76.8	17.40,	82.0
16.99,	70.2	20.69,	74.1	20.62,	79.8
19.11,	67.8	23.28,	71.7	23.20,	77.6
20.85,	66.2	25.39,	70.0	25.31,	75.8
22.30,	65.1	27.15,	68.7	27.07,	74.8
23.53,	63.8	28.64,	67.4	28.56,	74.0
24.58,	62.9	29.92,	67.2	29.84,	73.3
25.49,	62.4	31.03,	66.0	30.94,	72.7
26.29,	61.6	32.00,	65.3	31.91,	72.0
26.99,	61.0	32.86,	65.0	32.76,	71.5
$x_1 = 0.95712$					
4.44,	80.5	4.40,	83.4	4.50,	87.6
7.61,	76.6	7.54,	78.5	7.72,	80.8
9.99,	74.4	9.86,	76.0	10.13,	76.8
11.84,	72.9	11.73,	73.2	12.01,	74.0
13.32,	71.9	13.20,	72.0	13.51,	72.2
14.53,	70.8	14.40,	71.0	14.74,	70.5
15.54,	70.1	15.40,	69.8	15.76,	69.4
16.39,	69.5	16.25,	69.1	16.63,	68.6
17.12,	69.1	16.98,	68.5	17.37,	68.3
17.75,	68.7	17.61,	68.0	18.01,	66.9
18.30,	68.3	18.16,	67.4	18.57,	66.6

Contd.

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18.79,	68.1	18.64,	66.8	19.07,	66.0
$x_1 = 0.90657$					
1.57,	50.8	6.1	47.5	1.53,	70.6
2.69,	47.4	10.5	37.3	2.61,	67.1
3.53,	45.6	13.8	31.3	3.64,	63.8
4.19,	44.0	16.3	27.3	4.26,	61.8
4.71,	43.3	18.4	24.6	4.74,	60.0
5.13,	42.3	20.0	21.6	5.14,	58.9
5.49,	42.0	21.4	20.0	5.48,	58.0
5.79,	41.8	22.6	18.6	5.76,	57.3
6.05,	41.5	23.6	17.5	6.02,	57.0
6.28,	40.7	24.5	16.0	6.21,	56.0
6.48,	40.7	25.3	15.2	6.40,	55.2
6.65,	40.3	26.0	14.6	6.56,	55.4
Methanol + 1,4-Dioxane					
$x_1 = 0.96364$					
	LiCl		NaCl		KCl
10.11	102.1	10.22	97.3	9.52	100.4
17.33	100.5	17.51	91.2	16.32	95.8
22.75	99.5	22.98	89.1	21.42	92.9
26.96	98.6	27.23	86.7	25.39	91.1
30.30	98.1	30.63	85.1	28.57	89.5
33.09	97.7	33.42	84.1	31.17	88.3
35.39	97.4	35.74	83.1	33.33	87.5
37.34	97.2	37.70	82.3	35.16	86.8
39.01	96.9	38.38	81.8	36.73	86.1
40.45	96.7	40.48	81.3	38.09	85.9
41.71	96.5	42.12	80.9	39.28	85.3
42.83	96.4	43.25	80.5	40.33	85.1
$x_1 = 0.97747$					
9.68	96.8	9.84	98.3	7.89	96.9
16.60	93.3	46.86	93.6	13.52	92.9
21.79	91.1	22.13	90.6	17.75	90.5
25.82	89.5	26.23	88.8	21.04	88.5
29.05	88.5	29.51	87.1	23.67	87.0
31.69	87.3	32.19	85.8	25.82	86.1
33.89	86.9	34.43	84.9	27.61	85.5
35.75	86.2	36.32	84.1	29.13	84.5
37.35	85.7	37.94	83.6	30.43	84.1
38.73	85.5	39.34	83.1	31.56	83.6
39.94	85.2	40.57	82.6	32.55	83.1
41.01	84.9	41.65	82.3	33.42	82.7
$x_1 = 0.97747$					
3.62	87.9	3.59	89.5	3.85	91.4
6.20	84.7	6.16	85.9	6.60	87.0
8.14	82.7	8.09	83.5	8.66	84.6
9.65	81.2	9.59	81.8	10.26	82.6
10.85	80.2	10.79	81.2	11.54	81.6

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11.84	79.4	11.77	80.0	12.59	80.5
12.66	78.7	12.59	79.2	13.46	79.7
13.35	78.2	13.28	78.7	14.20	79.0
13.94	77.7	13.87	78.2	14.83	78.7
14.46	77.2	14.38	77.8	15.38	78.2
14.91	76.8	14.83	77.3	15.86	77.9
15.31	76.5	15.23	77.1	16.28	77.5

Table 3.

Values of derived conductance parameters (Λ_0 , K_A , R , Λ_{0n0} , σ) for alkali chlorides in mixed solvents at 298.15 K.

Mass% of Methanol	x_1	Λ_0 /S.cm ³ mol ⁻¹	K_A /dm ³ mol ⁻¹	R / Å	$\Lambda_0 n_0$	σ
LiCl / Methanol + Carbon Tetrachloride						
100.00	1	108.25±0.50	328.34±0.51	6.38	59.21	0.51
90.60	0.97885	106.79±0.71	492.40±0.71	6.14	60.57	0.71
82.31	0.95712	90.54±0.10	570.23±0.10	6.23	53.19	0.10
66.89	0.90657	60.22±0.18	642.41±0.18	6.43	38.77	0.18
NaCl / Methanol+ Carbon Tetrachloride						
100.00	1	111.85±0.79	253.35±0.79	6.73	61.18	0.50
90.60	0.97885	110.79±0.67	447.99±0.67	6.49	62.84	0.33
82.31	0.95712	98.23±0.33	460.91±0.10	6.58	57.71	0.10
66.89	0.90657	72.23±1.31	481.35±1.31	6.78	46.50	1.31
KCl / Methanol+ Carbon Tetrachloride						
100.00	1	113.77±.15	187.62±.15	7.11	62.22	0.15
90.60	0.97885	112.18±.31	344.69±.31	6.87	63.63	0.31
82.31	0.95712	103.22±.49	565.86±.49	6.96	60.64	0.49
66.89	0.90657	86.32±.34	776.44±.34	7.16	55.57	0.34
LiCl / Methanol + 1,4-Dioxane						
100.00	1	108.65±.51	328.34±.51	6.38	59.21	0.51
90.60	0.96364	107.35±.04	335.18±.04	6.43	59.99	0.04
82.31	0.92747	103.39±.11	341.24±.11	6.48	56.75	0.11
66.89	0.84752	96.85±.17	434.19±.17	6.69	55.05	0.17
NaCl / Methanol + 1,4-Dioxane						
100.00	1	111.85±.79	253.35±.79	6.73	61.18	0.79
90.60	0.96364	110.92±.26	241.87±.26	6.78	61.99	0.26
82.31	0.92747	106.21±.16	284.22±.16	6.83	58.29	0.16
66.89	0.84752	99.22±.28	370.31±.17	6.94	56.40	0.17
KCl / Methanol + 1,4-Dioxane						
100.00	1	113.77±0.15	187.62±0.15	7.11	62.22	0.15
90.60	0.96364	112.72±0.16	248.24±0.16	7.16	63.02	0.16
82.31	0.92747	108.63±0.21	254.63±0.21	7.21	59.62	0.21
66.89	0.84752	101.45±0.08	429.15±0.08	7.32	57.66	0.08

Electrical Conductance of Methanol + 1,4-Dioxane at 298.15 K.

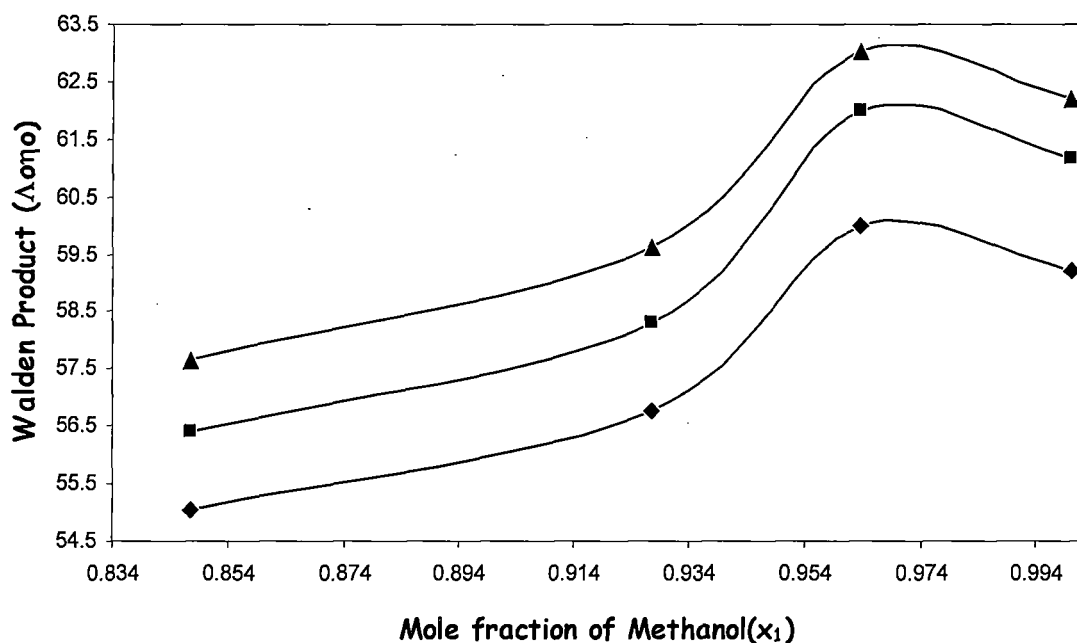


Fig1: Walden products for several alkali metal cations (♦ = LiCl, ■ = NaCl, ▲ = KCl) as a function of the mole fraction of methanol in Methanol-CCl₄ solvent mixture.

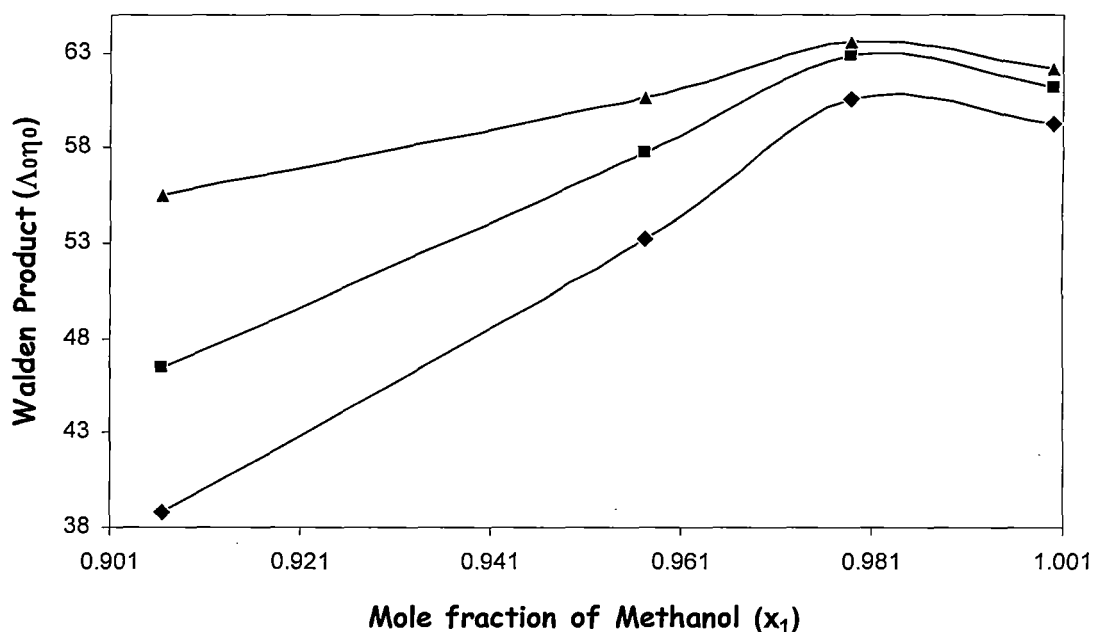


Fig2: Walden products for several alkali metal cations (♦ = LiCl, ■ = NaCl, ▲ = KCl) as a function of the mole fraction of methanol in Methanol- 1,4-DO solvent mixture.