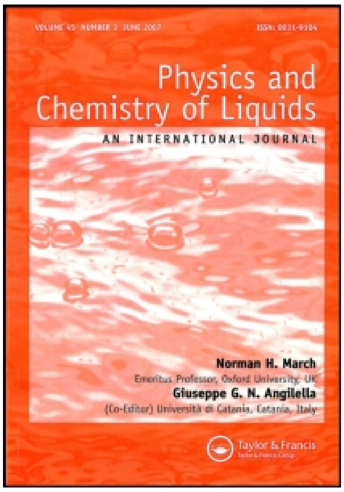

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Conductance and FTIR spectroscopic study of sodium tetraphenylborate in pure 1,3-dioxolane and isoamyl alcohol and their binary mixtures

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Systems of 1,3-dioxolane and isoamyl alcohol complexed with sodium tetraphenylborate ($NaBPh_4$) are examined using electrical conductance measurements and FTIR spectroscopy at 298.15 K. The conductance data has been analysed 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 ions (R). The observed molar conductivities were explained by the formation of ion-pairs ($M^+ + X^- \leftrightarrow MX$). Cation–anion interactions along with the hydrogen bonding interactions are investigated by evaluating the frequency shifts of the solvents in the pure state as well as their binary mixtures upon complexation with the salt.

Keywords: ion-pair; frequency shifts; sodium tetraphenylborate; 1,3-dioxolane; isoamyl alcohol

1. Introduction

Mixed solvent systems are used in a wide range of applications, and understanding the effect of changes in solvent composition remains a central problem in physical chemistry. Despite the accumulation of a considerable amount of information concerning the general behaviour of electrolytes in binary solvent mixtutres [1], little information is available on the electrochemical aspects of the electrolytes in the binary solvent mixtures of alcohols and cyclic ethers. Conductivity study is of great importance in obtaining information regarding the solvation and association behavior of ions in solution. Besides, FTIR spectroscopy has been one of the most convenient methods for investigating the ion–solvent interactions in electrolyte solutions [2]. The intermolecular interactions are of extreme importance in many fields of chemistry and molecular biology. The study of the effect of ion–solvent interaction and solvent–solvent interaction is also of much interest to solution chemists [3].

The systems chosen here for investigation have great industrial importance. 1,3-Dioxolane is used in pharmaceutical manufacturing, as substitute for chlorinated solvents, in lithium batteries, as copolymerisation agent, paint stripper, glue stabiliser, solubilising agent and manufacture of polyester membrane filters. Isoamyl alcohol is useful in gas chromatography. It can isolate high-quality RNA from even the hardest to isolate samples for immediate use in micro array application and also it is used in most DNA applications. Sodium tetraphenylborate has applications in catalyst identification,

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as a processing alternative for high-level waste, in high-performance liquid chromatography along with precipitation reactions [4–6].

In the present article, a detailed study has been done for sodium tetraphenylborate in pure as well as binary solvent mixtures of 1,3-dioxolane and *i*-amyl alcohol through conductance and FTIR spectroscopy, to elucidate the effect of the medium and particularly the role of specific ion–solvent interactions on the stability of the complexes.

2. Experimental

2.1. *Source and purity of samples*

1,3-Dioxolane ($C_3H_6O_2$, S.D. Fine Chemicals, 99% pure, containing 0.3% water and 0.005% peroxides) was used after further purification. It was dried with KOH and then distilled using xylene and PbO_2. Isoamyl alcohol ($C_5H_{12}O$, SRL, 99% pure, containing 0.2% water, 0.002% non-volatile matter and 0.001% peroxides) was purified by standard methods [7]. The purity of the solvents was checked by measuring their densities and viscosities at 298.15 K which were in good agreement with the literature values [8,9]. Sodium tetraphenylborate ($NaBPh_4, C_{24}H_{20}BNa$, Fluka, 99.5% pure) was crystallised from acetone–hexane and dried in a vacuum at 80°C before use. The materials finally obtained were found to be $>99.5\%$ pure.

2.2. *Method*

The conductance measurements were carried out in a systronic 308 conductivity bridge (accuracy ±0.01%) using a dip-type immersion conductivity cell, having cell constant $1.08\,cm^{-1}$. Determination of cell constant was based on 0.1 (M) aqueous KCl solution. The cell was calibrated by the method of Lind *et al.* [10]. The entire conductance data was reported at 1 KHz and was found to be ±0.3% precise. Due correction was made for the specific conductance of the solvent and solvent mixtures. The relative permittivity [11] of 1,3-dioxolane and *i*-amyl alcohol are 7.13 and 14.70, respectively. Eleven sets of solvent mixtures were prepared of varying compositions. The relative permittivity of the mixtures were obtained by the method suggested by Rohdewald *et al.* [12]. Solutions were a prepared by weight precise to ±0.02%. The weights were taken in a dehumidified room with utmost care on a Mettler electronic analytical balance (AG 285). The concentration range of electrolytes varied from $\sim (0.0725 \text{ to } 6.3530) \times 10^{-4}\,mol\,dm^{-3}$.

Infrared spectra was recorded on a 8300 FTIR spectrometer (Shimadzu-Japan) with a resolution of $\pm 0.25\,cm^{-1}$ in the region $4000–400\,cm^{-1}$ at room temperature (25°C) with 49–54% humidity. This KBr optics-based instrument records data in different modes (KBr Pellets, Nujol mull, non-aqueous solutions). The Spectrometer is equipped with a Michelson interferometer, single beam optics, Ge/KBr beam splitter, ceramic beam source, a high sensitivity pyroelectric detector (DLATGS) and He–Ne laser for data sampling. The spectra was properly normalised in order to take into account the effective number of absorbers.

Densities (ρ) were measured at 298.15 K with an Ostwald–Sprengel-type pycnometer having bulb volume of about $25\,cm^3$ and an internal diameter of the capillary of about 1 mm. Viscosities (η) were measured by means of a suspended Ubbelohde type viscometer. Calibration was done at 298.15 K with triply distilled water and purified tetrahydrofuran using density and viscosity values from the literature. The details of the methods and techniques for determination of the parameters were described earlier [13,14]. Measurements were made in a thermostated water bath maintained at 298.15 K ± 0.1 K. The precision in the density and viscosity measurements are $\pm 2 \times 10^{-4}\,\mathrm{kg\,m^{-3}}$ and $\pm 3 \times 10^{-4}$ Poise respectively.

3. Results and discussion

3.1. *Conductance*

The physical properties of the pure liquids and the solvent mixtures are given in Table 1. The experimental values of the molar conductances, Λ, against the respective concentration, c for $NaBPh_4$ salt in pure 1,3-dioxolane (1) and isoamyl alcohol (2) and their binary solvent mixtures over the whole mole fraction range at 298.15 K are recorded in Table 2. The conductance data has been analysed using the Fuoss conductance equation [15]. So with a given set of conductivity values ($c_j, \Lambda_j;\ j = 1, \dots, n$), three adjustable parameters, i.e., Λ_0, K_A and R are derived from the Fuoss equation. Here, Λ_0 is the limiting molar conductance, K_A is the observed association constant and R is the association distance, i.e., the maximum centre to centre distance between the ions in the solvent separated ion-pairs. There is no precise method [16] for determining the R value but in order to treat the data in our system, R value is assumed to be, $R = a + d$, where a is the sum of the crystallographic radii of the ions, which is 6.31 Å and d is the average distance corresponding to the side of a cell occupied by a solvent molecule. The distance, d (Å) is given by [15],

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

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

$$M_{av} = M_1 M_2/(W_1 M_2 + W_2 M_1) \tag{2}$$

where W_1 is the weight fraction of the first component of molecular weight M_1.

Table 1. Physical properties of pure solvents and the solvent mixtures.

Mole fraction of 1,3-dioxolane (x_1)	Density, $\rho \times 10^{-3}$ ($\mathrm{kg\,m^{-3}}$)	Viscosity, $\eta \times 10^2$ (Poise)	Relative permittivity, ε
0.0000	0.8069, ^{a}0.8071 [8]	3.8278, ^{a}3.4800 [8]	14.70
0.1168	0.8251	3.0166	13.94
0.2293	0.8447	2.5232	13.19
0.3377	0.8658	2.1743	12.43
0.4424	0.8877	1.8835	11.67
0.5434	0.9131	1.3664	10.92
0.6409	0.9399	0.9079	10.16
0.7352	0.9667	0.8074	9.40
0.8264	0.9952	0.7367	8.64
0.9146	1.0259	0.6474	7.89
1.0000	1.0586, ^{a}1.0586 [9]	0.5749, ^{a}0.5886 [9]	7.13

Note: ^{a}Literature value.

Table 2. Molar conductances, Λ and the corresponding concentration, c of sodium tetraphenylborate in pure 1,3-dioxolane (1) and isoamyl alcohol (2) and their binary solvent mixtures at 298.15 K.

$c \times 10^4$ ($\mathrm{mol\,dm^{-3}}$)	$\Lambda \times 10^4$ ($\mathrm{S\,m^2mol^{-1}}$)	$c \times 10^4$ ($\mathrm{mol\,dm^{-3}}$)	$\Lambda \times 10^4$ ($\mathrm{S\,m^2\,mol^{-1}}$)	$c \times 10^4$ ($\mathrm{mol\,dm^{-3}}$)	$\Lambda \times 10^4$ ($\mathrm{S\,m^2\,mol^{-1}}$)
$x_1 = 0.0000$, $\varepsilon = 14.70$		$x_1 = 0.1168$, $\varepsilon = 13.94$		$x_1 = 0.2293$, $\varepsilon = 13.19$	
0.630	9.52	0.568	12.61	0.480	16.55
1.599	8.50	1.322	12.15	1.218	15.99
2.310	7.79	1.910	11.92	1.759	15.73
2.854	7.25	2.359	11.72	2.173	15.59
3.283	6.95	2.714	11.63	2.500	15.47
3.630	6.58	3.001	11.52	2.765	15.37
3.917	6.43	3.238	11.44	2.983	15.28
4.158	6.35	3.438	11.39	3.167	15.18
4.363	6.34	3.607	11.35	3.323	15.10
4.540	6.23	3.754	11.31	3.458	15.03
4.695	6.16	3.881	11.25	3.575	14.99
4.830	6.09	3.993	11.23	3.679	14.95
$x_1 = 0.3377$, $\varepsilon = 12.43$		$x_1 = 0.4424$, $\varepsilon = 11.67$		$x_1 = 0.5434$, $\varepsilon = 10.92$	
0.395	19.64	0.323	25.73	0.260	30.41
1.002	18.81	0.821	23.64	0.660	28.17
1.447	18.48	1.186	22.86	0.954	27.26
1.788	18.21	1.464	22.40	1.178	26.74
2.056	18.02	1.685	22.02	1.355	26.34
2.274	17.83	1.863	21.74	1.499	25.96
2.454	17.71	2.010	21.54	1.617	25.66
2.605	17.60	2.134	21.37	1.717	25.46
2.734	17.51	2.239	21.21	1.801	25.26
2.844	17.46	2.330	21.11	1.874	25.13
2.941	17.36	2.409	21.00	1.938	25.03
3.026	17.30	2.479	20.94	1.994	24.88
$x_1 = 0.6409$, $\varepsilon = 10.16$		$x_1 = 0.7352$, $\varepsilon = 9.40$		$x_1 = 0.8264$, $\varepsilon = 8.64$	
0.237	33.91	0.169	35.35	0.133	35.58
0.600	30.81	0.395	32.94	0.287	33.43
0.867	29.64	0.570	31.93	0.414	31.85
1.071	28.85	0.704	30.96	0.512	31.25
1.232	28.32	0.810	30.49	0.589	30.56
1.363	27.89	0.896	29.92	0.651	30.10
1.470	27.54	0.966	29.70	0.703	29.74
1.561	27.29	1.026	29.44	0.746	29.36
1.638	27.11	1.077	29.17	0.783	29.13
1.704	26.93	1.120	28.92	0.815	28.97
1.762	26.73	1.158	28.83	0.842	28.73
1.813	26.64	1.192	28.61	0.867	28.62
$x_1 = 0.9146$, $\varepsilon = 7.89$		$x_1 = 1.0000$, $\varepsilon = 7.13$			
0.103	41.54	0.073	49.84		
0.221	39.43	0.158	46.35		
0.320	38.46	0.228	44.33		
0.395	37.46	0.281	43.35		
0.454	36.97	0.324	42.93		
0.503	36.61	0.358	42.46		

(*Continued*)

Table 2. Continued.

$c \times 10^4$ (mol dm^{-3})	$\Lambda \times 10^4$ (S m^{2}mol^{-1})	$c \times 10^4$ (mol dm^{-3})	$\Lambda \times 10^4$ (S m^2 mol^{-1})	$c \times 10^4$ (mol dm^{-3})	$\Lambda \times 10^4$ (S m^2 mol^{-1})
0.542	36.33	0.386	41.94		
0.576	35.96	0.410	41.70		
0.604	35.76	0.430	41.36		
0.629	35.48	0.448	40.87		
0.650	35.24	0.463	40.82		
0.669	34.99	0.476	40.73		

Thus, the Fuoss conductance equation may be represented as follows:

$$\Lambda = p[\Lambda_0(1 + R_X) + E_L], \tag{3}$$

$$p = 1 - \alpha(1 - \gamma), \tag{4}$$

$$\gamma = 1 - K_A c \gamma^2 f^2, \tag{5}$$

$$-\ln f = \beta k / 2(1 + K_R), \tag{6}$$

$$\beta = e^2 / \varepsilon k_B T, \tag{7}$$

$$K_A = K_R/(1 - \alpha) = K_R(1 + K_S), \tag{8}$$

where R_X is the relaxation field effect, E_L is the electrophoretic countercurrent, k^{-1} is the radius of the ion atmosphere, ε is the relative permittivity of the solvent or solvent mixture, e is the electron charge, c is the molarity of the solution, k_B is the Boltzmann constant, K_A is the overall pairing constant, K_S is the association constant of contact-pairs, K_R is the association constant of solvent-separated pairs, γ is the fraction of solute present as unpaired ion, α is the fraction of contact pairs, f is the activity coefficient, T is the absolute temperature and β is twice the Bjerrum distance.

The computations are performed on a computer using the program suggested by Fuoss. The initial Λ_0 values for the iteration procedure are obtained from Shedlovsky extrapolation of the data [17,18]. Now, we input for the program, the no. of data, n, followed by ε, η (viscosity of the solvent mixture), initial Λ_0 value, T, ρ (density of the solvent mixture), mole fraction of the first component, molecular weights, M_1 and M_2 along with c_j, Λ_j values where $j = 1, 2, \ldots, n$ 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 minimise the standard deviation, σ, whereby

$$\sigma^2 = \sum [\Lambda_{j(\text{calc})} - \Lambda_{j(\text{exp})}]^2 / n - 2, \tag{9}$$

for a sequence of R values and then plotting σ against R, the best-fit R corresponds to the minimum in σ versus R curve. So an approximate sum is made over a fairly wide range of R values using a 0.1 increment to locate the minimum. But no significant minima is found in

Table 3. Fuoss-conductance parameters for sodium tetraphenylborate in pure 1,3-dioxolane (1) and isoamyl alcohol (2) and their binary solvent mixtures at 298.15 K.

X_1	R^a (Å)	$\Lambda_0{}^b \times 10^4$ ($S\,m^2\,mol^{-1}$)	$K_A{}^c$ ($dm^3\,mol^{-1}$)	$\sigma\%^d$
0.0000	11.97	11.91 ± 0.42	4216.47	0.10
0.1168	11.89	13.42 ± 0.21	338.98	0.02
0.2293	11.81	16.93 ± 0.20	11.13	0.16
0.3377	11.73	20.56 ± 0.10	373.22	0.12
0.4424	11.66	27.67 ± 0.14	1655.93	0.12
0.5434	11.58	32.77 ± 0.11	1894.94	0.14
0.6409	11.49	37.18 ± 0.17	2903.73	0.09
0.7352	11.42	39.04 ± 0.15	3752.46	0.06
0.8264	11.34	39.35 ± 0.11	5381.83	0.19
0.9146	11.26	45.31 ± 0.52	4146.15	0.08
1.0000	11.18	53.93 ± 0.37	8150.31	0.28

Notes: [a] Association distance.
[b] Limiting molar conductance.
[c] Association constant.
[d] Standard deviation.

the σ–R curves, thus the R value is assumed to be $R = a + d$, with terms having usual significance [15]. Finally, the corresponding Λ_0 and K_A values are obtained which are reported in Table 3 along with R and σ for the binary mixtures of the tetraphenylborate salt.

3.1.1. *Limiting molar conductance*

It is observed here that the limiting molar conductance, Λ_0, is minimum in pure isoamyl alcohol and maximum in pure 1,3-dioxolane, i.e. the value gradually increases as the amount of 1,3-dioxolane increases in the binary solvent mixtures. The increase in Λ_0 means an increase in the mobility of the ions which is due to a decrease in the viscosities of the mixtures [19]. Thus, the experimental results obtained here for the binary mixtures are in accordance with the Walden's rule. Pure 1,3-dioxolane has maximum mobility of the ions as it has the easiest flow. Since the resistance to the flow of liquid mixture becomes highest in pure isoamyl alcohol, we find minimum Λ_0 at this point. The results are in good agreement with those obtained by Das *et al.* [20] and Srivastava *et al.* [21].

3.1.2. *Association constant*

The association constant, K_A at first decreases and gives a minima at $x_1 = 0.2293$, then it gradually increases. The K_A of pure isoamyl alcohol (component 2) is less than that of pure 1,3-dioxolane (component 1) owing to their difference in relative permittivities, ε. The salt, $NaBPh_4$, showed a larger association in the cyclic diether medium. This is expected as pure (1) has lower ε (7.13) than the pure alcohol ($\varepsilon = 14.7$). The deviations (σ) point towards an ionic association in the pure and mixed solvent media.

3.1.3. *Walden's product*

The Walden's product, $\Lambda_0\,\eta$ [22,23], is also calculated for the various solvent compositions and the results have been depicted in Figure 1. The Walden's product, $\Lambda_0^{calc}\eta$ and $\Lambda_0^{exp}\eta$,

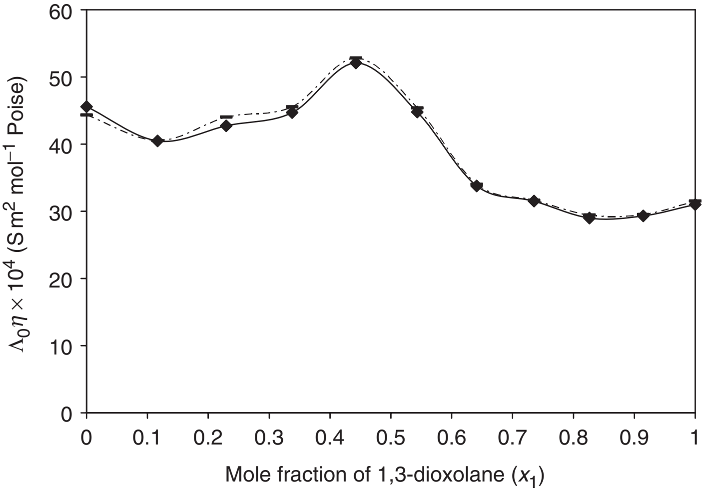


Figure 1. Walden's product, $\Lambda_0^{\text{calc}}\ \eta$ (·······) and $\Lambda_0^{\text{exp}}\ \eta$ (—◆—) of sodium tetraphenylborate in pure 1,3-dioxolane (1) and isoamyl alcohol (2) and their binary solvent mixtures against the mole fraction of 1,3-dioxolane (x_1) at 298.15 K.

both calculated and experimental, have been compared and are observed in excellent agreement with each other. Figure 1 indicates that Walden's product is higher for $NaBPh_4$ in the alcohol-rich mixtures rather than the cyclic diether-rich mixtures with a maximum at $x_1 = 0.4424$. The variation of the Walden product reflects the change of solvation [24]. The solvation of $Na^+BPh_4^-$ ions becomes weak in the presence of the alcohol molecules but 1,3-dioxolane solvates the $Na^+BPh_4^-$ ions, specifically resulting in greater ion-solvent interaction. The maximum point indicates preferential solvation of the ions by both the solvents. Further; $x_1 = 0.4424$ is the specific point of interaction for the cylic diether and alcohol molecules predominated by H-bonding interactions as shown by our earlier work [25].

3.1.4. *Gibbs' energy of ion-pair formation*

Figure 2 predicts the nature of the curves for the Gibbs' energy of ion-pair formation, ΔG^0 for the binary mixtures studied here. ΔG^0 is given by the relationship [26],

$$\Delta G^0 = -RT \ln K_{\text{A}}. \tag{10}$$

The curve indicates that the tendency for ion-pair formation of $Na^+BPh_4^-$ ions decreases significantly with an increase in the association factor, K_{A} for the electrolyte in the solvent medium and vice versa. Therefore, at $x_1 = 0.2293$ the tendency for ion-pair formation is maximum. There is a greater degree of ion-pair formation and a lower extent of association when the solvent medium contains more isoamyl alcohol molecules, attributing to its higher ε than 1,3-dioxolane which in fact has minimum ΔG^0 in pure state.

Alcohol molecules self associate [25] very strongly (–OH···OH– interaction) whereas the cyclic diether molecules self associate (–O···O– interaction) rather marginally. This has

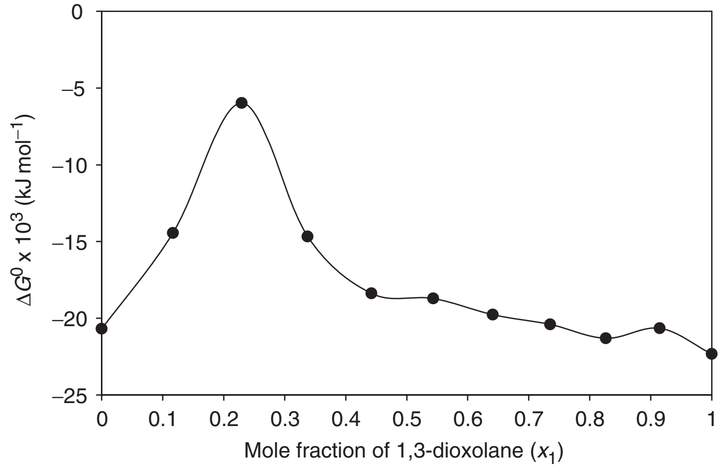


Figure 2. Gibbs energy of ion-pair formation, ΔG^0 of sodium tetraphenylborate in pure 1,3-dioxolane (1) and isoamyl alcohol (2) and their binary solvent mixtures against the mole fraction of 1,3-dioxolane (x_1) at 298.15 K.

a dramatic influence on the thermophysical properties studied. Isoamyl alcohol acting as Lewis acid and 1,3-dioxolane as Lewis base, gives favourable intermolecular complexation through H-bonding (–O–O···H–O–). The ions in the electrolytic solution are represented by the equilibria [21]:

$$Na^+ + BPh_4^- \leftrightarrow (Na^+ \cdots BPh_4^-) \leftrightarrow Na^+BPh_4^- \leftrightarrow NaBPh_4.$$

(Cation) (Anion) (Solvent separated pair) (Contact pair) (Neutral molecule).
Similar types of work have been done by Hazra *et al.* [27,28].

3.2. *Infrared spectroscopy*

FTIR spectra [29,30] has been used as supporting evidence for the study of the bond formation due to ion–solvent and solvent–solvent interactions.

3.2.1. *O–H stretching vibrations*

At first, the IR of the solvent mixtures (represented as SM) of isoamyl alcohol and 1,3-dioxolane are studied. Figure 3a (SM 1) shows the nature of bands and peaks in pure isoamyl alcohol. A broad O–H stretching vibration is obtained for intermolecular H-bonding at 3317.3 cm^{-1} which in the presence of the Na$^+$ and BPh$_4^-$ increases to 3348.2 cm^{-1} (represented as S 1) and so on. The O–H band is a composite of a large number of unresolved bands, corresponding to different modes of association of alcohol molecules. As the alcohol is diluted with 1,3-dioxolane, the peak value starts increasing and is observed to be 3379.1 cm^{-1} for $x_1 = 0.4424$ (Figure 3e-SM 5).Thereafter, the broadening of the bands starts decreasing and a sharp peak is found at 3525.6 cm^{-1} for $x_1 = 0.9146$ (Figure 3j-SM 10). On adding ether, which acts as H-acceptor, the band arising

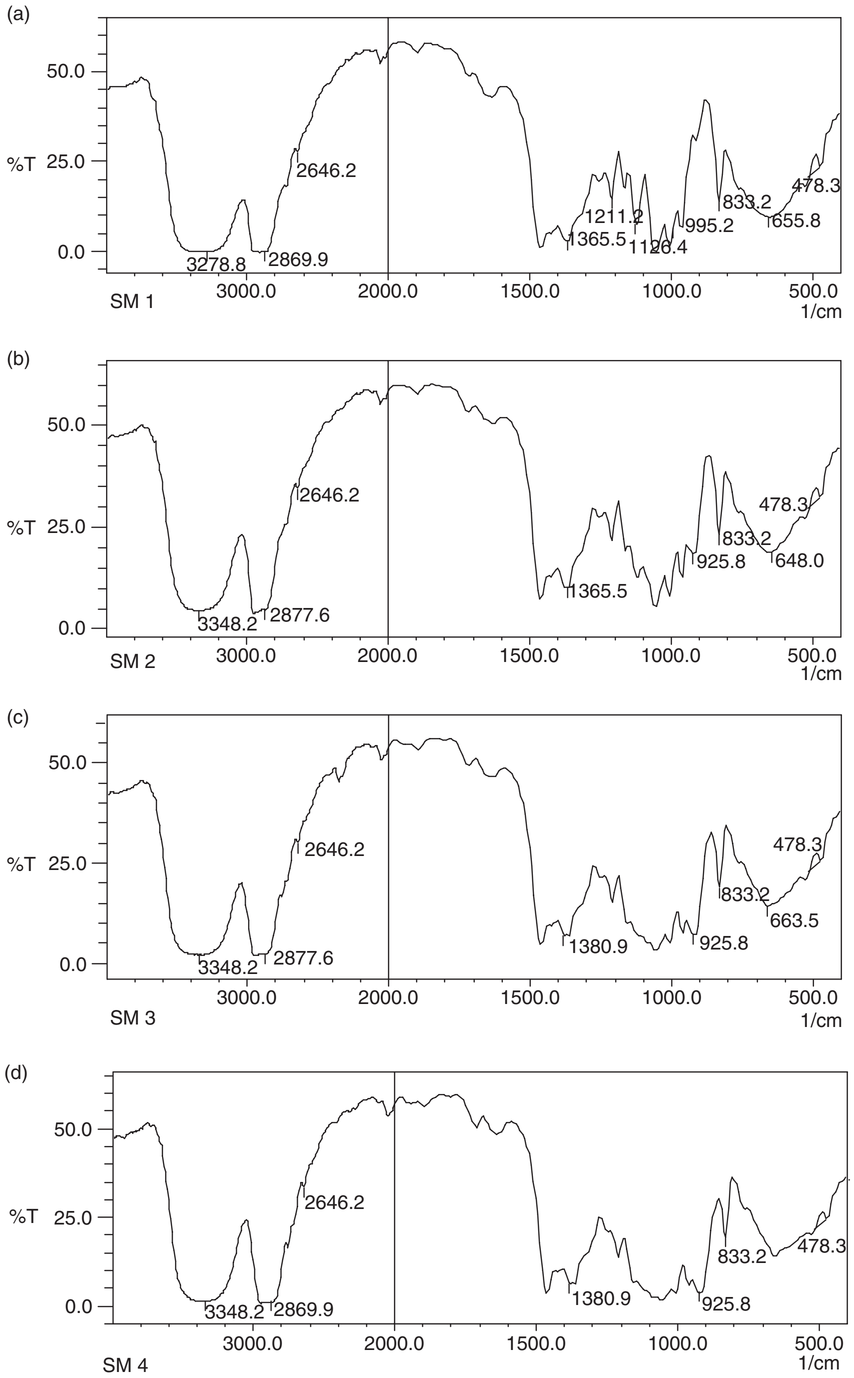


Figure 3. Infrared spectra (represented as SM) of the pure and binary solvent mixtures of 1,3-dioxolane (1) and isoamyl alcohol (2) at 298.15 K. (a) $x_1 = 0.0000$ (b) $x_1 = 0.1168$ (c) $x_1 = 0.2293$ (d) $x_1 = 0.3377$ (e) $x_1 = 0.4424$ (f) $x_1 = 0.5434$ (g) $x_1 = 0.6409$ (h) $x_1 = 0.7352$ (i) $x_1 = 0.8264$ (j) $x_1 = 0.9146$ (k) $x_1 = 1.0000$.

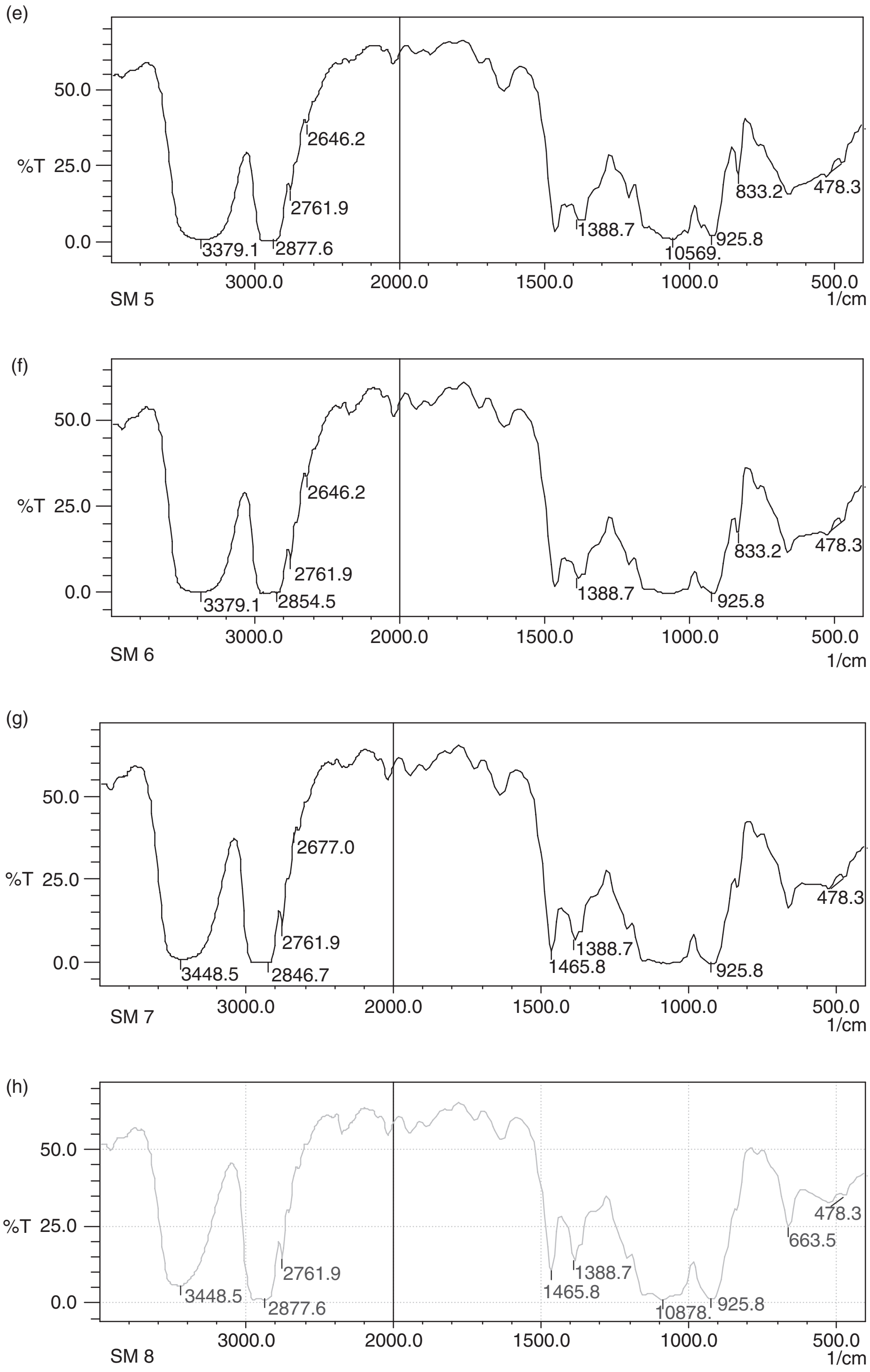


Figure 3. Continued.

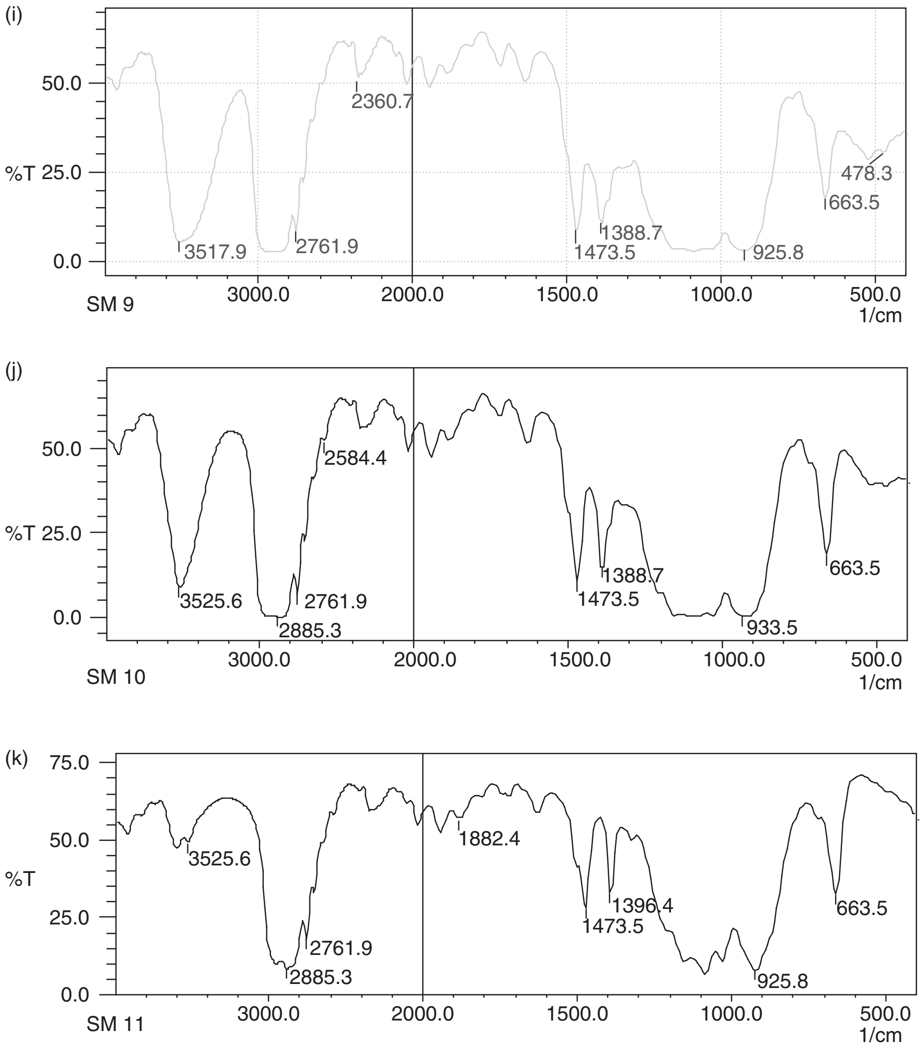
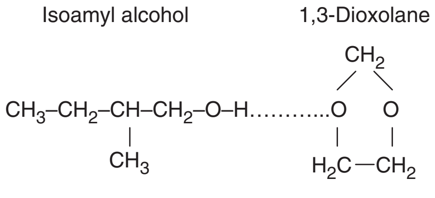


Figure 3. Continued.

from intermolecular H-bonding becomes stronger due to association between alcohol and ether molecules.



Another weak peak seems to appear to the left of the broad band in the region 3800–3900 cm^{-1} as the proportion of diether molecules increases in the mixture. This may be the free non-H-bonded O–H stretching peak which is known to occur when alcohol is dissolved in another solvent. As x_1 increases, the broad intermolecular H-bonded band is reduced considerably. The intermolecular H-bonding weakens the O–H bond, thereby shifting the band to lower frequency (lower energy) in pure 1,3-dioxolane. Similar effects of H-bonding have been studied by Bellamy *et al.* [31,32].

The broad peaks in the region 2700–3000 cm^{-1} appeared for the symmetric –CH$_3$ stretching vibrations which resolves further in presence of ether molecules. However, when the salt, NaBPh$_4$ is added to the solvent systems, it is observed that these peaks split up into two finer peaks, one at 2954.7 and other at 2877.6 cm^{-1} representing the asymmetric and symmetric –CH$_3$ stretching vibrations, respectively (Figure 4a). Further, at $x_1 = 0.4424$ (Figure 4e, S 5), resolution is more prominent. In $x_1 = 1.0$ (Figure 4k), the intensity of the symmetric peak becomes greater than the asymmetric one.

3.2.2. *O–H deformation vibrations*

This gives peaks within the range 1300–1470 cm^{-1}. The participation of the O–H group in the H-bonding increases the frequency of the vibration which initially appears at 1465 cm^{-1} overlapping with the –CH$_2$– bending peaks and increases slightly as the proportion of the cyclic diether increases in the mixture.

3.2.3. *C–O–H stretching vibrations*

Strong absorption peaks are observed in Figure 3a in the region from 1000 to 1250 cm^{-1} which is assigned to be the characteristic vibration of the C–O–H group. The peak at 1056.9 cm^{-1} represents [33] the saturated primary aliphatic alcohol, which is isoamyl alcohol. In addition to this, an O–H in plane bending absorption is found at 1365.5 cm^{-1} that overlaps with the C–H bending vibration of the methyl group. As 1,3-dioxolane is added to the system, the sharp peaks starts disappearing into wide bands. Although the peak 1056.9 cm^{-1} disappears completely at $x_1 = 0.5434$ in SM 6 (Figure 3f), but Figure 4f shows the peak at 1087.8 cm^{-1} in $x_1 = 0.5434$ (S 6) due to predominance of ion–solvent interaction effect over solvent–solvent interaction. However, this peak reappears at $x_1 = 0.7352$ in SM 8 (Figure 3h) as a broad band with a higher value of 1087.8 cm^{-1} but in presence of Na$^+$ and BPh$_4^-$ ions, it appears as a sharp peak in S 8 (Figure 4h).

3.2.4. *C–O–H bending vibrations*

This bending vibration coupled with H–C–H bending vibrations yield weak and broad peaks in the 1220–1470 cm^{-1} region which are located under the more strongly absorbing –CH$_3$ bending peaks at 1365.5 cm^{-1} (Figure 3a). This value starts increasing in presence of the diether molecules and is 1396.4 cm^{-1} at $x_1 = 1.0$.

3.2.5. *C–O–C stretching vibrations*

There are broad peaks in the range of 1000–1200 cm^{-1} for the asymmetrical stretching mode of the C–O–C bond in saturated aliphatic ethers [34], i.e. at 1100 cm^{-1} for pure 1,3-dioxolane (Figure 3k).The symmetrical vibration occurs at a frequency of 925.8 cm^{-1} which appears in presence of the cyclic diether (Figure 3b onwards). As the alcohol molecules come into play, the peaks disappear to give broad bands in this region that is the Na$^+$ and BPh$_4^-$ ions interacting more with the diether molecules, giving finer and sharper

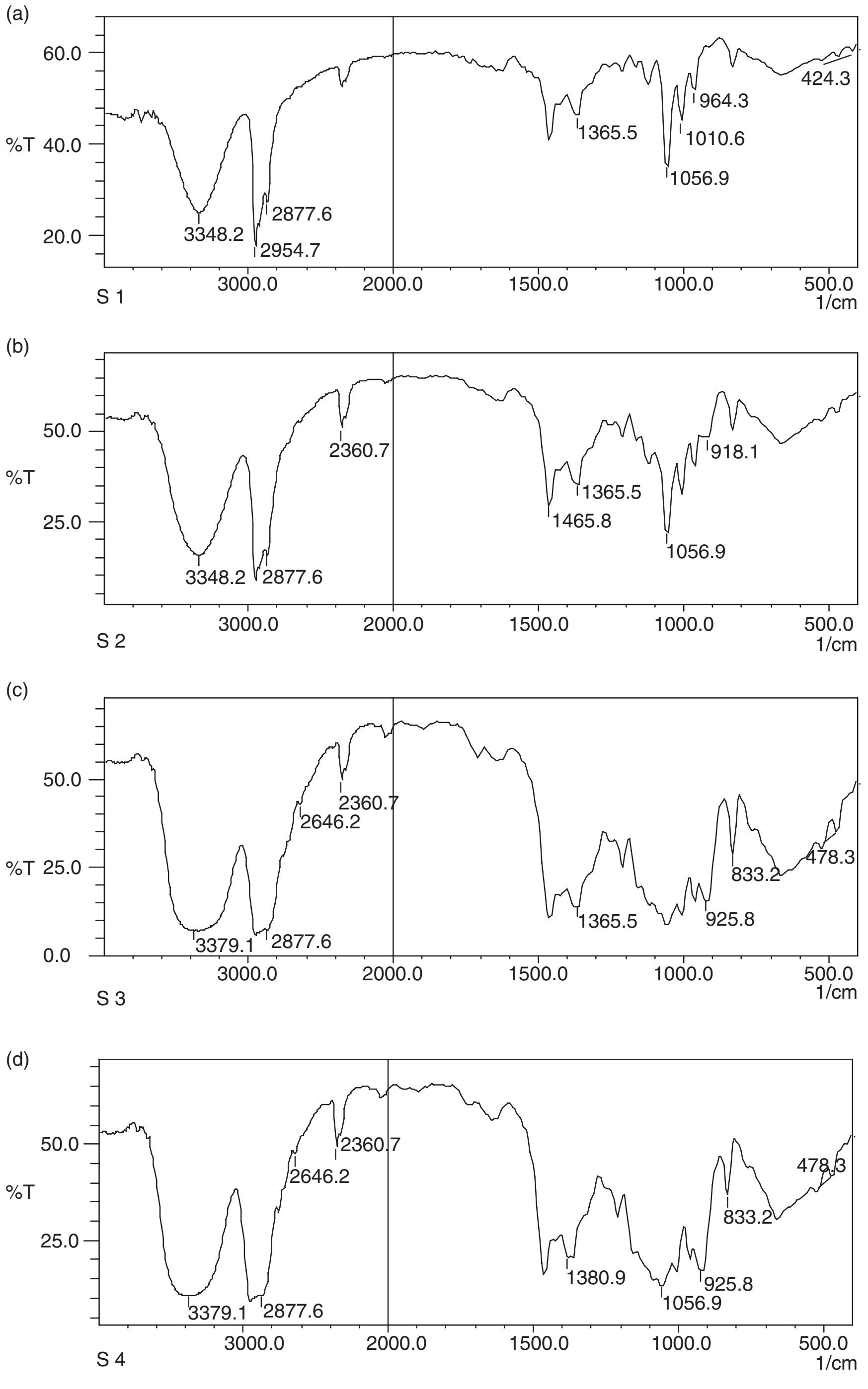


Figure 4. Infrared spectra (represented as S) of sodium tetraphenylborate in pure and binary solvent mixtures of 1,3-dioxolane (1) and isoamyl alcohol (2) at 298.15 K. (a) $x_1 = 0.0000$ (b) $x_1 = 0.1168$ (c) $x_1 = 0.2293$ (d) $x_1 = 0.3377$ (e) $x_1 = 0.4424$ (f) $x_1 = 0.5434$ (g) $x_1 = 0.6409$ (h) $x_1 = 0.7352$ (i) $x_1 = 0.8264$ (j) $x_1 = 0.9146$ (k) $x_1 = 1.0000$.

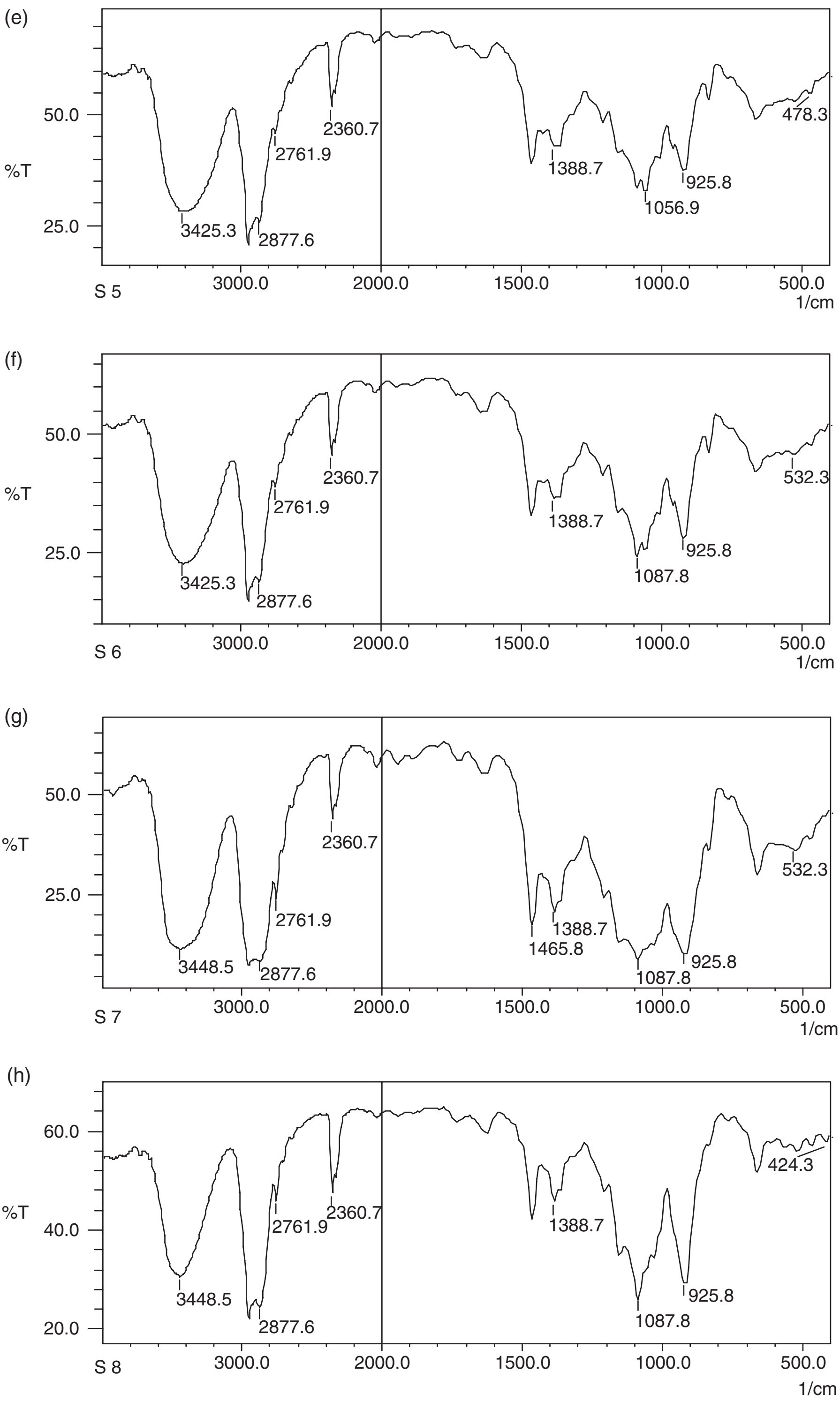


Figure 4. Continued.

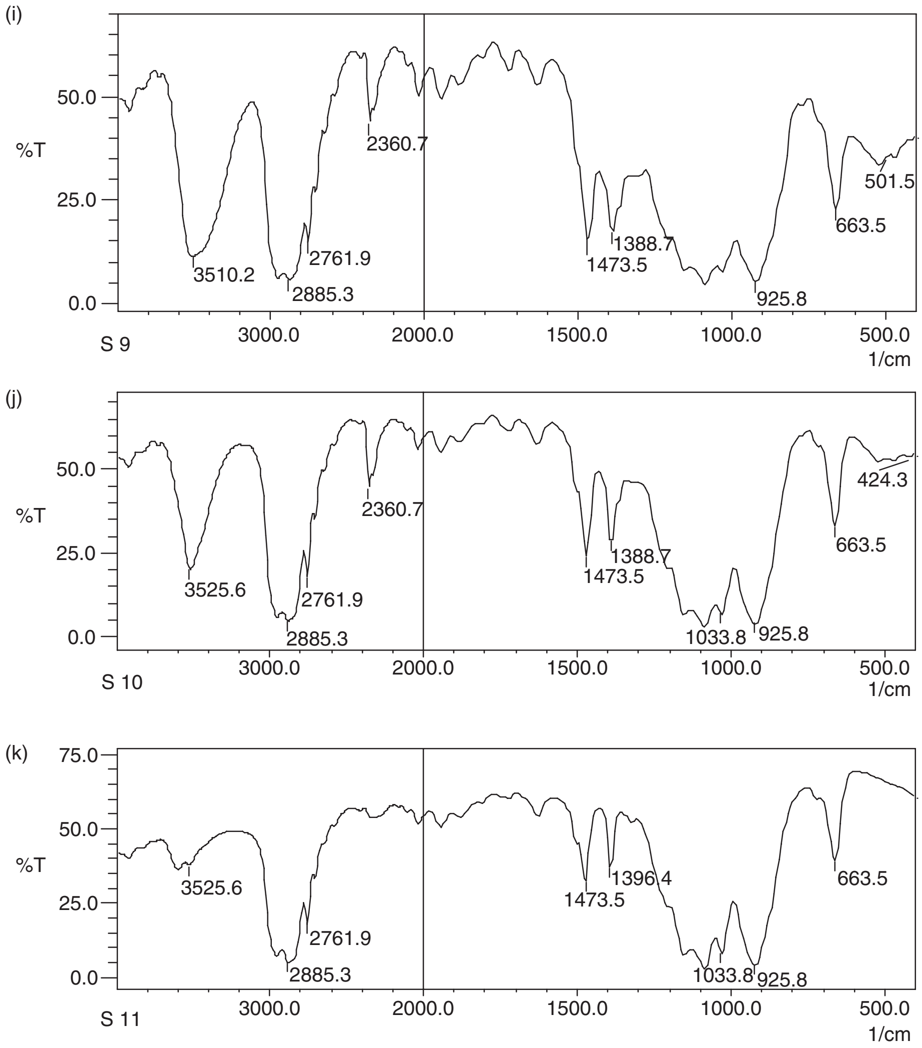


Figure 4. Continued.

peaks in this region as the proportion of 1,3-dioxolane increases in the mixture. Fawcett *et al.* [35] have studied the ion–solvent interaction with FTIR spectrum using similar types of salts and solvents.

4. Conclusion

The conductometric and FTIR study of 1,3-dioxolane, isoamyl alcohol and sodium tetraphenylborate revealed a lot about the ion–solvent and solvent–solvent interactions operating in this system. It is observed here that the mobility of the ions gradually increases as the amount of 1,3-dioxolane increases in the binary solvent mixtures. The salt, $NaBPh_4$ showed a larger association in the cyclic diether medium. In other words, there is a greater degree of ion-pair formation and a lower extent of association when the solvent a medium contains more isoamyl alcohol molecules. Further, the solvation of $Na^+BPh_4^-$ ions becomes weak in the presence of the alcohol molecules, but 1,3-dioxolane solvates the $Na^+BPh_4^-$ ions specifically resulting in greater ion–solvent interaction. On adding ether which acts as a H-acceptor, the band arising from intermolecular H-bonding becomes stronger due to association between alcohol and ether molecules. Thus, Na^+ and BPh_4^- ions are observed to interact more with the diether molecules as revealed by the spectrum analysis.

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