Equations 3 and 5 have been used to calculate the solvation numbers. It is remarkable that the values of solvation numbers as calculated from the equation (5) in Table I and those from Wada's relation (3) in Table II agree very closely with each other.

The progressive decrease in solvation numbers with concentration is usually ascribed to the change over to the secondary solvation. However, this situation is not observed in these cases because with the change in concentration there is very small variation in the values of the solvation numbers as is evident from the results given in Table I.

Glossary

C	concentration, mol l.$^{-1}$
β	adiabatic compressibility of solution
β_0	adiabatic compressibility of solvent
Z	specific acoustic impedance
R	molar sound velocity
$\phi_{(k)}$	apparent molal compressibility
n_s	solvation number
c	sound velocity, m s^{-1}
ρ	density, g cm^{-3}
n_1	number of moles of solvent
n_2	number of moles of solute
V	volume of solution
V_1^0	molar volume of solvent

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Molal Volumes of Lithium, Sodium, and Potassium Chloride in Multicomponent Electrolyte Solutions (LiCl–NaCl–KCl–Aqueous Dioxane)

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Molal volumes of LiCl, NaCl, and KCl have been evaluated in multicomponent solutions of aqueous dioxane (30%, 50%, 70%) from the density data of the system LiCl–NaCl–KCl–aqueous dioxane, at different temperatures. The results have been interpreted in terms of ion–solvent interaction.

During the recent years considerable activity has been noticed regarding thermodynamic and transport properties of multicomponent electrolyte solutions (*4, 7*). Studies in mixed solvents have so far been restricted to one or two salt systems only. Mixed solvent multicomponent systems are important as they approach very close to biological fluids. In aqueous dioxane it is considered that dioxane acts more or less like an inert dilutent (*7*) and water takes part in the equilibrium process as in pure water. However, at higher content of dioxane in aqueous dioxane solvent, viz., as the dielectric constant of the mixed solvent decreases, the interionic forces are strong enough to lead to some form of ion pairing (*4*). These types of ion–ion or ion–solvent interactions can be interpreted by the partial molar volume studies.

Experimental Section

The alkali chlorides used in this experiment were of Analar grade and they were used without further purification. Conductivity water prepared by the usual method (*3*) was used for making the aqueous dioxane mixture by weight. Dioxane (G.R.) was purified by refluxing over sodium metal for 5-6 h followed by distillation.

The densities were measured with the help of an apparatus similar to the hydrostatic balance described by Ward and Millero (*10*). A 116-g glass float of volume 26.17 cm^3 was suspended into a glass sample cell of 200 cm^3 capacity. The cell has a bakelite top with a hole in the center and is placed in a temperature bath controlled to better than ±0.025 °C. The densities of the solutions were calculated from the equation:

$$d - d^0 = (W^0 - W)/V_f \tag{1}$$

where d and d^0 are the densities of the solution and pure water, respectively, W and W^0 are the weights of the float in the solution and pure water, respectively, and V_f is the volume of the float. The accuracy was checked by measuring density of pure dioxane at 30 °C. Our value $d = 1.022\ 46$ is in excellent agreement with the literature value (*9*) $d = 1.022\ 30$. The difference in weight of the float in water and dioxane was $\pm 3.0 \times 10^{-5}$ g and it gives a good precision in the measurement of the density.

Results and Discussion

The densities of the following systems were measured in 50% aqueous dioxane at 30, 40, and 50 °C: I, LiCl (C_i) + NaCl (0.01 N) + KCl (0.01 N) + aqueous dioxane; II, LiCl (0.01 N) + NaCl (C_i) + KCl (0.01 N) + aqueous dioxane; III, LiCl (0.01 N) + NaCl (0.01 N) + KCl (C_i) + aqueous dioxane; where C_i is the concentration of the respective salt. Densities were also measured for the systems I, II, and III in 30 and 70% aqueous dioxane at 40 °C. The densities as a function of concentration C_i are given in Tables I–III.

The partial molar volumes $\overline{V}_i$ for the ith salt in these systems have been calculated by using eq 2

$$\overline{V}_i = \frac{M_i - 1000H_i}{\rho - \sum_{j=1}^{q} H_jC_j} \tag{2}$$

Table I. Density of System I

Concn of LiCl C_i (g equiv l.$^{-1}$)	% composition of dioxane	Density d (g ml^{-1})		
		30 °C	40 °C	50 °C
0.1	30		1.026 93	
0.2			1.028 76	
0.3			1.030 61	
0.5			1.034 31	
0.7			1.037 98	
0.1	50	1.022 5		
0.3		1.025 92		
0.5		1.029 32		
0.7		1.032 73		
0.9		1.036 2		
0.1	50		1.011 00	
0.3			1.015 69	
0.5			1.020 45	
0.7			1.025 18	
0.9			1.029 89	
0.1	50			1.001 10
0.3				1.006 65
0.5				1.012 16
0.7				1.018 70
0.9				1.023 21
0.1	70		1.022 95	
0.2			1.025 4	
0.3			1.027 88	
0.4			1.030 35	
0.5			1.032 75	
0.8[a]				

[a] At these concentrations two immiscible layers in the solution are observed.

Table II. Density of System II

Concn of NaCl C_i (g equiv l.$^{-1}$)	% composition of dioxane	Density d (g ml^{-1})		
		30 °C	40 °C	50 °C
0.1	30		1.022 35	
0.15			1.024 75	
0.20			1.027 15	
0.25			1.029 53	
0.30			1.031 96	
0.1	50		1.028 51	
0.2			1.031 72	
0.3			1.034 92	
0.5			1.041 35	
0.7			1.047 76	
0.1	50	1.036 50		
0.2		1.039 53		
0.3		1.042 7		
0.5		1.049 01		
0.7		1.055 22		
0.1	50			1.017 88
0.2				1.021 29
0.3				1.024 78
0.5				1.031 82
0.7				1.038 78
0.1	70		1.028 77	
0.2			1.031 72	
0.3			1.034 68	
0.4			1.037 61	
0.5[a]				

[a] At these concentrations two immiscible layers in the solution are observed.

Table III. Density of System III

Concn of KCl C_i (g equiv l.$^{-1}$)	% composition of dioxane	Density d (g ml^{-1})		
		30 °C	40 °C	50 °C
0.2	30		1.020 43	
0.3			1.023 2	
0.5			1.031 95	
0.7			1.039 53	
0.9			1.047 12	
0.1	50	1.034 85		
0.2		1.038 87		
0.3		1.042 85		
0.5		1.050 83		
0.7		1.058 77		
0.1	50		1.023 85	
0.3			1.033 92	
0.5			1.044 07	
0.7			1.054 15	
0.9			1.064 07	
0.1	50			1.012 31
0.3				1.023 65
0.5				1.034 79
0.7				1.045 91
0.9				1.056 85
0.1	70		1.024 82	
0.2			1.026 9	
0.3			1.028 98	
0.4			1.031 05	
0.5[a]				

[a] At these concentrations two immiscible layers in the solution are observed.

Table IV. Values of ϕ_V^0 for the *i*th Salt in the Systems I, II, and III at Various Temperatures and Compositions of Dioxane

System	Temp (°C)	ϕ_V^0 (ml mol^{-1})		
		30% dioxane	50% dioxane	70% dioxane
LiCl in system I	30		24.41	
	40	23.82	18.91	17.06
	50		15.83	
NaCl in system II	30		27.53	
	40	11.64	25.81	27.74
	50		24.89	
KCl in system III	30		33.54	
	40	34.18	22.75	53.37
	50		17.32	

where

$$H_i = (\delta\rho / C_i)_{\mathrm{T,P,C_k}} \tag{3}$$

and M_i is the molecular weight of the salt i, C_i the molar concentration of the salt, ρ the density of the system, and q is the total number of solutes. The molar volumes thus calculated are given in Tables I–III.

The partial molal volumes evaluated for the *i*th salt are found to remain more or less constant with the change in concentration of the *i*th salt. Plots of $\overline{V}_i$ vs. concentration are straight lines and on extrapolation of the plots to zero concentration give $\overline{V}_i^0$ which varied from $\overline{V}_i$ values at a concentration in the third decimal place only and we have taken the mean of $\overline{V}_i$ equal to $\overline{V}_i^0$ and hence equal to the apparent molal volume, ϕ_V^0, at infinite dilution (*7*). The average value of ϕ_V^0 for different salts in different systems is given in Table IV.

The temperature dependence of the ϕ_V^0 of LiCl, NaCl, and KCl in different systems can be expressed by the equations:

$$\phi_V^0 = 59.04 - 1.54t + (1.3 \times 10^{-2})t^2 \text{ (system I)} \tag{4}$$

$$\phi_V^0 = 37.20 - 0.44t + (3.8 \times 10^{-3})t^2 \text{ (system II)} \tag{5}$$

$$\phi_V^0 = 97.27 - 2.93t + (2.7 \times 10^{-2})t^2 \text{ (system III)} \tag{6}$$

The decrease in the ϕ_V^0 of LiCl in 50% dioxane for system I with increasing temperature can be attributed to the increase in the electrostriction partial molal volume $\bar{V}^0$ (elect) at higher temperature. Estimation of $\phi_V{}^0$ values from eq 4 shows that $\phi_V{}^0$ of LiCl in system I goes through a minimum around 60 °C which shows that $\bar{V}^0$ (elect) decreases at temperatures above 60 °C. In other words, $\bar{V}^0$ (int), the intrinsic partial molal volume, is more dominant than $\bar{V}^0$ (elect). The apparent molal expansibilities, $\phi_E{}^0 = (\delta\phi_V{}^0/\delta t)$ calculated from eq 4 between 0 and 100 °C, indicate increases with increase in temperature and this is contrary to the behavior of most common electrolytes in that $\phi_E{}^0$ decreases with increasing temperature. This may be attributed to (*i*) the presence of strong ion-ion interaction, (*ii*) the increase in association of ions by the addition of one electrolyte to a solution, and (iii) the decrease of overall solvation of ions in a multicomponent electrolyte solution. Using the reasoning of Hepler (*6*) one can attribute this behavior to the ability of lithium chloride to act as a structure maker.

The, $\phi_V{}^0$, values for lithium chloride in system I decrease with increasing content of dioxane at 40 °C. In aqueous dioxane (*1*), inorganic ions are preferentially solvated by dioxane, and dioxane-water mixtures form an associated complex in the liquid state by the attachment of two water molecules to the oxygen atoms of dioxane through hydrogen bonding. Since lithium salts are more solvated (*5*), the decrease with increasing content of dioxane indicates the encagement of the lithium chloride ions in the vacant space of the associated complex of water-dioxane. Since it behaves as a structure maker, there is no possibility of its breaking the structure of aqueous dioxane and, therefore, it may not be interacting with the associated solvent molecules. Lithium ions have the tendency of interacting with the water molecules and this interaction goes on decreasing due to decrease in water molecules with the increase in the dioxane content and more and more of the ions start getting into the void space of the structure of the solvent and there is a gradual decrease in the $\phi_V{}^0$ values of lithium chloride in system I.

The effect of temperature on $\phi_V{}^0$ for sodium chloride in system II with increasing temperature can be attributed to the same reasoning as applied to system I and the minimum is again obtained at 60 °C. According to Hepler (*6*), the positive value of $(\delta^2\phi_V{}^0/\delta t^2)$ for a salt shows the structure-making character of the salt. On comparing the magnitudes of LiCl in system I and of NaCl in system II, we find that lithium chloride is more of a structure maker than sodium chloride in their respective systems. The apparent molal expansibilities, $\phi_E{}^0 =' \delta\phi_V{}^0/\delta t$ calculated from eq 5 between 0 and 100 °C, show that it increases with increase in temperature and it may be attributed to the nonelectrolytic behavior as this behavior is very much common for nonelectrolytes or tetraalkylammonium salts. In the case of system II, we find that $\phi_V{}^0$ increases with increase in the dioxane content. This has been attributed to the greater ionic size of the sodium ion and the vacant site in the solvent containing the molecules of the associated complex is not of sufficient dimensions for the salt to be trapped in and the electrolyte remains outside the void space. This void space goes on increasing with the increase in the content of the dioxane and, therefore, it is expected the $\phi_V{}^0$ will increase with increasing content of dioxane because sodium chloride ions go on occupying space outside the solvent matrix.

The effect of temperature on the $\phi_V{}^0$ of KCl in system III can be explained similar to that of system I and II. The evaluation of $\phi_V{}^0$ from eq 6 in the temperature range suggests that the minimum in this approaches at 60 °C. Helper's reasoning suggests (*6*) that potassium chloride in system III behaves like a structure maker. The effect of dioxane on the $\phi_V{}^0$ values in the case of system III suggests that a minimum is observed around 50% dioxane mixture at 40 °C and this may be attributed to the increasing dominance of the intrinsic partial molal volume over the electrostriction partial molal volume.

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Isopiestic Determination of the Osmotic Coefficients of Aqueous $CaCl_2$ Solutions at 25 °C

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The isopiestic molalities of $CaCl_2$ and H_2SO_4 solutions have been determined at 25 °C for $CaCl_2$ concentrations between 2.6 and 8.8 mol kg^{-1}. The osmotic coefficients of the $CaCl_2$ solutions were calculated using available osmotic coefficients for H_2SO_4. These results can be combined with other published data to give accurate osmotic and activity coefficients for $CaCl_2$ solutions.

One of the most widely used methods for the determination of water activities of aqueous solutions is the isopiestic method. This method consists of allowing solutions of various electrolytes to reach thermodynamic equilibrium, through the vapor phase, with standard solutions whose water activities should be accurately known as a function of concentration.

$CaCl_2$ has become one of the most important isopiestic standards since this use was suggested by Stokes (*4*). Below 3 mol kg^{-1} (water activities between 0.75 and 1.00) this salt has been extensively studied by isopiestic comparison to NaCl and KCl solutions, by freezing point depression measurements, and by use of electromotive force and diffusion coefficient measurements. Most of these data are in good agreement. Above 3 mol kg^{-1}, the $CaCl_2$ osmotic coefficients are based mainly on Stokes' isopiestic comparison to H_2SO_4 (*4*). Very few reliable