

Molal Volumes of LiCl, NaCl & KCl in Multicomponent Electrolyte Solutions (LiCl-NaCl-KCl-H₂O)

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Molal volume (\bar{v}_i) of the *i*th component, viz. LiCl, NaCl or KCl in multicomponent solutions has been evaluated from the density data of the system LiCl-NaCl-KCl-H₂O at different electrolyte concentrations and at different temperatures. The \bar{v}_i is found to be independent of concentration and hence is equal to the partial molal volume at infinite dilution. Inferences have been drawn about the extent of solute-solvent interaction in comparison to ion-ion interaction.

DURING the recent years considerable activity has been noticed regarding thermodynamic and transport properties of multicomponent electrolyte solutions^{1,2}. These solutions are found in numerous processes in chemical industry and play an important role in the physiological processes of body fluids, and cell equilibrium, therefore their study is important both from theoretical and practical viewpoint. The partial molal volume of one electrolyte, in multicomponent systems, will depend on the concentration of the other electrolytes. In such situations the electrostrictions of the solvent will change. However, the intrinsic volume of the ion will remain the same². Evaluation of the partial molal volume in a multicomponent system were carried out with a view to finding how the partial molal volume of individual electrolyte changes with concentration and temperature.

Materials and Methods

LiCl, NaCl and KCl of Analar grade were used as such and their solutions were prepared in conductivity water³.

The density was measured with the help of a double capillary pycnometer (25 ml capacity) as described elsewhere⁴. The pycnometer was calibrated with the conductivity water and values of carbon tetrachloride and chloroform were measured as: 1.58377 ± 0.00025 and 1.47048 ± 0.00026 g ml⁻¹ respectively. These values are comparable with the literature values⁵.

Results and Discussion

The densities for the following systems: (I) LiCl (*C_i*)-NaCl (0.01*N*)-KCl (0.01*N*)-H₂O; (II) LiCl (0.01*N*)-NaCl (*C_i*)-KCl (0.01*N*)-H₂O; and (III) LiCl (0.01*N*)-NaCl (0.01*N*)-KCl (*C_i*)-H₂O in which the concentration of the component *C_i* varies from 0.01-0.1*N* were measured at 30°, 40° and 50° and the values are given in Table 1.

The density of the systems I-III vary linearly with the concentration *C_i* and as well as with the total concentration *C_t* of the system at all tempe-

ratures. The partial molal volume for each system at different concentrations are evaluated from the following expression⁶:

$$\bar{V}_i = \frac{M_i - 1000 H_i}{\rho - \sum_{j=1}^q H_j C_j}$$

where

$$H_i = \left(\frac{\partial \rho}{\partial C_i} \right)_{T,P,C_k \neq i}$$

and *M_i* is the molecular weight of the solute *i*, *C_i* is the molar concentration of the solute *i*, ρ is the density of the respective system, and *q* is the total number of solutes. The partial molal volumes

TABLE 1 — VALUES OF DENSITY FOR SYSTEMS I-III AT DIFFERENT TEMPERATURES

<i>C_i</i> (g eq. litre ⁻¹)	Density (g ml ⁻¹) at		
	30°	40°	50°
SYSTEM I			
0.01	0.99675	0.99255	0.98880
0.03	0.99701	0.99308	0.98937
0.05	0.99742	0.99361	0.98995
0.07	0.99775	0.99417	0.99053
0.09	0.99812	0.99473	0.99110
SYSTEM II			
0.01	0.99675	0.99255	0.98880
0.03	0.99777	0.99412	0.99121
0.05	0.99859	0.99492	0.99198
0.07	0.99940	0.99557	0.99282
0.09	1.00036	0.99653	0.99365
SYSTEM III			
0.01	0.99675	0.99255	0.98880
0.03	0.99805	0.99434	0.99001
0.05	0.99877	0.99538	0.99105
0.07	0.99978	0.99648	0.99211
0.09	1.00062	0.99758	0.99347

TABLE 2 — VALUES OF PARTIAL MOLAL VOLUME FOR THE *i*TH SALT AT INFINITE DILUTION (\bar{V}_i°) FOR THE SYSTEMS I, II AND III AT DIFFERENT TEMPERATURES

System	Temperature (°C)	\bar{V}_i° (ml mole ⁻¹)
LiCl. in system I	30	25.00
	40	14.87
	50	13.14
NaCl in system II	30	14.06
	40	18.91
	50	16.77
KCl in system III	30	31.50
	40	21.02
	50	20.58

thus evaluated for the *i*th salt are found to be constant in the concentration range (0.01-0.01N) studied. Since \bar{V}_i is found to be independent of the concentration C_i , it can be taken to be equal to \bar{V}_i° the partial molal volume at infinite dilution. The values of \bar{V}_i° are given in Table 2.

\bar{V}_i° the partial molal volume at infinite dilution is equivalent to ϕ_v° , the apparent molal volume at infinite dilution⁷. Quite recently Gopal *et al.*⁸ and Millero⁹ have shown that the dependence of ϕ_v° on temperature is a very good tool for

the study of ion-solvent interactions. The values of \bar{V}_i° indicate strong solute-solvent interactions. The negative temperature coefficients for systems I and III suggest that at lower temperatures solute-solvent interaction is more than the ion-ion interaction and the situation is reversed at high temperatures. In the case of system II, however, greater solute-solvent interaction is observed at 40°.

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