Isothermal Diffusion Coefficients of H₂O-LiCl-NaCl-KCl & DMSO-LiCl-NaCl-KCl Systems

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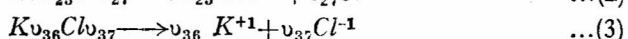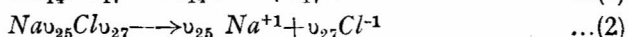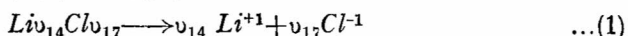Department of Chemistry, Himachal Pradesh University, Simla 171001

Non-equilibrium thermodynamics has been used to evaluate phenomenological and diffusion coefficients at 25° for the systems H₂O-LiCl-NaCl-KCl and DMSO-LiCl-NaCl-KCl at concentrations varying from 1 to 9 × 10⁻⁵ mole ml⁻¹. Onsager's reciprocity relations have been found to hold good. The diffusion behaviour of these systems is explained in the light of electrostatic interactions between ions and in terms of the mobility of ions.

AQUEOUS solutions of electrolytes show some of the largest solute-solute and solute-solvent[1] interactions during flow processes. In recent years, transport properties, viz. electrical conductance[2], viscous flow[3,4] of electrolytes in dilute solutions have received considerable attention. However, in dilute solutions, diffusion results are apparently non-existent for electrolytes in organic solvents. This is partly due to the viability of accurate measurements at low concentrations. Diffusion studies of multicomponent systems are of considerable importance for biological transport[5] as these systems approach very close to biological fluids. One of the characteristic features of a biological membrane is its selective permeability by which it may accept or reject, retain or excrete substances. This is accomplished in part by passive transport which depends primarily on diffusion[6]. Therefore, diffusion coefficient is the main transport coefficient useful in interpreting biological transport. In the present paper, diffusion coefficients and phenomenological coefficients for the systems: H₂O-LiCl-NaCl-KCl and DMSO-LiCl-NaCl-KCl are reported. Dimethyl sulphoxide (DMSO) is an extremely important biological liquid and has manifold properties and estimations in DMSO and H₂O are made for the study of comparative behaviour of these solvents.

Theoretical

The evaluation of the diffusion coefficients, and phenomenological coefficients has been done as described earlier[7,8]. However, the important steps for carrying out these evaluations are summarized below:

Since the concentration of these salts is of the order of 10⁻⁵ mole/ml in water and DMSO, these salts can be safely assumed to exist in the ionized state as follows:

$$Li\upsilon_{14}Cl\upsilon_{17} \longrightarrow \upsilon_{14} Li^{+1} + \upsilon_{17}Cl^{-1} \qquad ...(1)$$

$$Na\upsilon_{25}Cl\upsilon_{27} \longrightarrow \upsilon_{25} Na^{+1} + \upsilon_{27}Cl^{-1} \qquad ...(2)$$

$$K\upsilon_{36}Cl\upsilon_{37} \longrightarrow \upsilon_{36} K^{+1} + \upsilon_{37}Cl^{-1} \qquad ...(3)$$

where the subscripts 1, 2, 3....7 refer to LiCl, NaCl, KCl, Li⁺, Na⁺, K⁺ and Cl⁻ respectively. The coefficient υ_{ij} $(i = 1—3; j = 4....7)$ refers to the stoichiometric content of each ion with respect to each salt. Now, according to non-equilibrium thermodynamics, isothermal diffusion for a salt is described by the following relations:

$$(J_i)_0 = -\sum_{j=1}^{3} (L_{ij})_0 \, grad. -(\mu_j) \quad (i = 1, 2, 3) \qquad ...(4)$$

and

$$(J_i)_0 = -\sum_{j=1}^{3} (D_{ij})_0 \, grad. \, C_j \quad (i = 1, 2, 3) \qquad ...(5)$$

where $(L_{ij})_0$ is the phenomenological coefficient, $(D_{ij})_0$ the diffusion coefficient, $(J_i)_0$ flow of the neutral salts, μ_j the chemical potential of the salt and C_j the concentration of the salt.

Considering diffusion as a one-dimensional process, and on applying the theory of thermodynamics of irreversible processes as in the case of bio-fluids[8], we get the following equations for the flows of neutral salts:

$$(J_1)_0 = \upsilon_{14}^{-1} \sum_{j=1}^{3} \sum_{l=4}^{7} X_j \, a_{lj}\Omega_{4l} \qquad ...(6)$$

$$(J_2)_0 = \upsilon_{25}^{-1} \sum_{j=1}^{4} \sum_{l=4}^{7} X_j a_{lj}\Omega_{5l} \qquad ...(7)$$

$$(J_3)_0 = \upsilon_{36}^{-1} \sum_{j=1}^{4} \sum_{l=4}^{7} X_j \, a_{lj} \, \Omega_{6l} \qquad ...(8)$$

where X_j is the thermodynamic force and

$$\Omega_{il} = (L_{il})_0 - \frac{\sum\limits_{j=4}^{7} \sum\limits_{k=4}^{7} (L_{ij})_0 \, a_{j4} \, a_{k4} \, (L_{kl})_0}{\sum\limits_{m=4}^{7} \sum\limits_{n=4}^{7} a_{m4} (L_{mn})_0 \, a_{n4}}$$
$$(i = 4....7) \quad ...(9)$$

for $(L_{ij})_0 \neq 0$ $(i, j = 4, 5, 6, 7)$ at all concentrations and a's as:

$$a_{41} = a_{42} = a_{43} = 0, \; a_{44} = 1$$

$$a_{51} = -\frac{\upsilon_{27}}{\upsilon_{25}\upsilon_{17}}, a_{52} = \frac{1}{\upsilon_{25}}, a_{53} = 0, \; a_{54} = \frac{\upsilon_{14}\upsilon_{27}}{\upsilon_{17}\upsilon_{25}} \quad ...(10)$$

$$a_{61} = -\frac{\upsilon_{37}}{\upsilon_{36}\upsilon_{17}}, a_{62} = 0, \; a_{63} = \frac{1}{\upsilon_{36}}, a_{64} = \frac{\upsilon_{14}\upsilon_{37}}{\upsilon_{17}\upsilon_{36}}$$

$$a_{71} = \frac{1}{\upsilon_{17}}, a_{72} = 0, \; a_{73} = 0, \; a_{74} = -\frac{\upsilon_{14}}{\upsilon_{17}}$$

The phenomenological coefficients $(L_{ij})_0$ come out as:

$$(L_{1j})_0 = \upsilon_{14}^{-1} \sum_{j=1}^{3} \sum_{l=4}^{7} a_{lj} \, \Omega_{4l} \qquad \ldots(11)$$

$$(L_{2j})_0 = \upsilon_{25}^{-1} \sum_{j=1}^{3} \sum_{l=4}^{7} a_{lj} \, \Omega_{5l} \qquad \ldots(12)$$

$$(L_{3j})_0 = \upsilon_{30}^{1-} \sum_{j=1}^{3} \sum_{l=4}^{7} a_{lj} \, \Omega_{6l} \qquad \ldots(13)$$

Accordingly Eq. (9) can be written as:

$$\Omega_{il} = (L_{il})_0 \; \delta_{il} - \frac{(L_{ii})_0 \, a_{i4} \, a_{l4} \, (L_{ll})_0}{\sum_{k=4} a_{k4}^2 \, (L_{kk})_0} \qquad (i, l = 4 \ldots 7) \qquad \ldots(14)$$

where δ_{il} is the Kronecker δ, i.e. $\delta_{il} = 1$ for $i = 1$ and $d_{il} = 0$ for $i \neq 1$. Wendt[7] has related the straight coefficients $(L_{ii})_0$ to their respective ionic limiting equivalent conductivity λ_i° as:

$$(L_{ii})_0 = \frac{\lambda_i^\circ C_i}{(|Z|F^2 \times 10^7)} \qquad \ldots(15)$$

Further, the solvent fixed diffusion coefficients $(D_{ij})_0$ are related to the solvent-fixed phenomenological coefficients $(L_{ij})_0$ by

$$(D_{ij})_0 = \sum_{k=1}^{3} (L_{ik})_0 \, \mu_{kj} \qquad (i, j = 1, 2, 3) \qquad \ldots(16)$$

Thus by knowing μ_{kj} and $(L_{ik})_0$, we can estimate $(D_{ij})_0$. Values of $(L_{ik})_0$ for the neutral solutes have been estimated using the Eqs (15), (14), (11-13) and μ_{kj} have been estimated from the following expression:

$$\mu_{ik} = RT \left[\frac{\upsilon_{i4}}{C_1} + \frac{\upsilon_{i5}}{C_2} + \frac{\upsilon_{i6}}{C_3} + \frac{\upsilon^{i7}\upsilon_{k7}}{\upsilon_{17}C_1 + \upsilon_{27}C_2 + \upsilon_{37}C_3} \right]$$
$$(i, k = 1, 2, 3) \qquad \ldots(17)$$

which has been derived from the equation[7]

$$\mu_i = \mu_i^\circ + RT \ln \prod_{j=4}^{7} (y_j C_j) \, \upsilon_{ij} \quad (i = 1, 2, 3) \qquad \ldots(18)$$

where y_j is the activity coefficient of the ion j and μ_i° is the chemical potential at the standard state for neutral salt i. In deriving Eq. (17), it is assumed that

$$\frac{\delta \ln (y_\pm)_i}{\delta C_j} = 0 \quad (i, j = 1, 2, 3) \qquad \ldots(19)$$

where $(y_\pm)_i$ is the mean ionic activity coefficient for the neutral solute.

Results and Discussion

The values of $(L_{ij})_0$ and $(D_{ij})_0$ for these systems, given in Tables 1-4 show that the cross-coefficients are equal and therefore, Onsager's reciprocity relations[9,10] hold good in these systems. Further, it is found that the cross-coefficients have appreciable magnitude and cannot be neglected in comparison with the straight coefficients. The magnitude of the cross-term diffusion coefficients, D_{ij}, depend on three factors, viz. concentration and the mobility of component i, and the force produced by a unit concentration gradient of component, j. It is observed that as the concentration of the component i is increased, the value of D_{ij} decreases. This may be due to the fact that the mobility of component i decreases with increase in concentration. In the system LiCl-NaCl(c)-KCl-H_2O, as the concentration of NaCl increases, the diffusion coefficient of NaCl decreases. On the other hand, the diffusion coefficient of LiCl and KCl increases in magnitude with the increase in concentration of NaCl. This points out that the force produced by a unit concentration gradient of NaCl is increased which further increases the mobility of the potassium and lithium ions.

Another interesting feature of the values of the cross-diffusion coefficient is that at any particular concentration:

$$D_{11} = D_{12} = D_{13}; \quad D_{21} = D_{22} = D_{23}; \quad D_{31} = D_{32} = D_{33}$$

This may be attributed to the fact that the force produced by a unit concentration gradient of LiCl or NaCl or KCl is same. This is also supported by the fact that the increase in the value of the diffusion coefficient of NaCl with the increase in the concentration of KCl is the same as that with the concentration increase of LiCl. A similar behaviour is observed for the other two salts also.

When the concentration of the three salts is the same in the system, it is observed that the diffusion coefficient of KCl has the maximum magnitude and that of the LiCl has the minimum. It may be interpreted that in these multicomponent electrolyte solutions K^+ has the largest mobility and

TABLE 1 — VALUES OF PHENOMENOLOGICAL COEFFICIENT FOR THE SYSTEM LiCl-NaCl-KCl-H_2O

Concentration			$(L_{ij})_0 \times 10^{22}$								
LiCl $C_1 \times 10^5$	NaCl $C_2 \times 10^5$	KCl $C_3 \times 10^5$	$(L_{11})_0$	$(L_{12})_0$	$(L_{13})_0$	$(L_{21})_0$	$(L_{22})_0$	$(L_{23})_0$	$(L_{31})_0$	$(L_{32})_0$	$(L_{33})_0$
1·0	1·0	1·0	36·125	−5·292	−7·492	−5·292	46·709	−10·064	−7·492	−10·064	61·944
3·0	1·0	1·0	101·216	−10·087	−14·281	−10·087	49·460	−6·170	−14·281	−6·170	67·456
5·0	1·0	1·0	160·327	−12·256	−17·351	−12·256	50·641	−4·498	−17·351	−4·498	69·824
7·0	1·0	1·0	217·740	−13·500	−19·112	−13·500	51·318	−3·539	−19·112	−3·539	71·181
1·0	1·0	1·0	36·125	−5·292	−7·492	−5·292	46·709	−10·064	−7·492	−10·064	61·944
1·0	3·0	1·0	37·731	−9·406	−4·438	−9·406	123·551	−17·887	−4·438	−17·887	67·751
1·0	5·0	1·0	38·392	−11·238	−3·182	−11·238	193·614	−21·371	−3·182	−20·897	70·077
1·0	7·0	1·0	38·761	−12·261	−2·479	−12·261	261·437	−23·317	−2·476	−23·317	71·476
1·0	1·0	1·0	36·125	−5·292	−7·492	−5·292	46·709	−10·064	−7·492	−10·064	61·944
1·0	1·0	3·0	37·898	−2·911	−12·812	−2·911	49·908	−17·210	−12·812	−17·210	161·133
1·0	1·0	5·0	38·554	−2·029	−14·884	−2·029	51·093	−19·994	−14·884	−19·994	248·130
1·0	1·0	7·0	38·905	−1·557	−15·993	−1·557	51·726	−21·484	−15·993	−21·484	332·084

TABLE 2 — VALUES OF THE PHENOMENOLOGICAL COEFFICIENTS FOR THE SYSTEM LiCl-NaCl-KCl-DMSO

Concentration			$(L_{ij})_0 \times 10^{22}$								
LiCl $C_1 \times 10^5$	NaCl $C_2 \times 10^5$	KCl $C_3 \times 10^5$	$(L_{11})_0$	$(L_{12})_0$	$(L_{13})_0$	$(L_{21})_0$	$(L_{22})_0$	$(L_{23})_0$	$(L_{31})_0$	$(L_{32})_0$	$(L_{33})_0$
1·0	1·0	1·0	11·018	−1·564	−1·581	−1·564	13·622	−2·017	−1·581	−2·017	13·749
3·0	1·0	1·0	29·957	−2·800	−2·912	−2·800	14·392	−1·238	−2·912	−1·238	14·536
5·0	1·0	1·0	47·643	−3·463	−3·501	−3·463	14·733	−0·893	−3·501	−0·893	14·885
7·0	1·0	1·0	64·895	−3·792	−3·834	−3·792	14·925	−0·699	−3·834	−0·699	15·082
1·0	1·0	1·0	11·018	−1·564	−1·581	−1·564	13·622	−2·017	−1·581	−2·017	13·749
1·0	3·0	1·0	11·516	−2·786	0·939	−2·786	36·189	−3·591	−0·939	−3·592	14·577
1·0	5·0	1·0	11·726	−3·302	−0·668	−3·302	57·025	−4·275	−0·668	−4·257	14·927
1·0	7·0	1·0	11·847	−3·586	−0·518	−3·586	77·294	−4·624	−0·518	−4·624	15·120
1·0	1·0	1·0	11·018	−1·564	−1·581	−1·564	13·622	−2·017	−1·581	−2·017	13·749
1·0	1·0	3·0	11·517	−0·927	−2·812	−0·927	14·434	−3·586	−2·812	−3·586	36·487
1·0	1·0	5·0	11·727	−0·659	−3·330	−0·659	14·776	−4·247	−3·330	−4·247	57·470
1·0	1·0	7·0	11·843	−0·511	−3·616	−0·511	14·964	−4·612	−3·616	−4·612	77·878

TABLE 3 — VALUES OF DIFFUSION COEFFICIENT FOR THE SYSTEM LiCl-NaCl-KCl-H$_2$O

Concentration			$(D_{ij})_0 \times 10^5$								
LiCl $C_1 \times 10^5$	NaCl $C_2 \times 10^5$	KCl $C_3 \times 10^5$	$(D_{11})_0$	$(D_{12})_0$	$(D_{13})_0$	$(D_{21})_0$	$(D_{22})_0$	$(D_{23})_0$	$(D_{31})_0$	$(D_{32})_0$	$(D_{33})_0$
1·0	1·0	1·0	0·771	0·771	0·771	1·036	1·036	1·036	1·467	1·467	1·467
3·0	1·0	1·0	0·613	0·613	0·613	1·154	1·154	1·154	1·634	1·634	1·634
5·0	1·0	1·0	0·524	0·524	0·524	1·203	1·203	1·203	1·703	1·703	1·703
7·0	1·0	1·0	0·472	0·472	0·472	1·231	1·231	1·231	1·743	1·743	1·743
1·0	1·0	1·0	0·771	0·771	0·771	1·036	1·036	1·036	1·467	1·467	1·467
1·0	3·0	1·0	0·865	0·865	0·865	0·821	0·821	0·821	1·646	1·646	1·646
1·0	5·0	1·0	0·902	0·902	0·902	0·721	0·721	0·721	1·717	1·717	1·717
1·0	7·0	1·0	0·922	0·922	0·922	0·666	0·666	0·666	1·753	1·753	1·753
1·0	1·0	1·0	0·771	0·771	0·771	1·036	1·036	1·036	1·467	1·467	1·467
1·0	1·0	3·0	0·871	0·871	0·871	1·170	1·170	1·170	1·251	1·251	1·251
1·0	1·0	5·0	0·909	0·909	0·909	1·262	1·262	1·262	1·100	1·100	1·100
1·0	1·0	7·0	0·928	0·928	0·928	1·279	1·279	1·279	1·058	1·058	1·058

TABLE 4 — VALUES OF DIFFUSION COEFFICIENT FOR THE SYSTEM LiCl-NaCl-KCl-DMSO

Concentration			$(D_{ij})_0 \times 10^5$								
LiCl $C_1 \times 10^5$	NaCl $C_2 \times 10^5$	KCl $C_3 \times 10^5$	$(D_{11})_0$	$(D_{12})_0$	$(D_{13})_0$	$(D_{21})_0$	$(D_{22})_0$	$(D_{23})_0$	$(D_{31})_0$	$(D_{32})_0$	$(D_{33})_0$
1·0	1·0	1·0	0·260	0·260	0·260	0·332	0·332	0·332	0·336	0·336	0·336
3·0	1·0	1·0	0·224	0·224	0·224	0·353	0·353	0·353	0·357	0·357	0·357
5·0	1·0	1·0	0·208	0·208	0·208	0·363	0·363	0·363	0·367	0·367	0·367
7·0	1·0	1·0	0·199	0·199	0·199	0·368	0·368	0·368	0·372	0·372	0·372
1·0	1·0	1·0	0·260	0·260	0·260	0·332	0·332	0·332	0·336	0·336	0·336
1·0	3·0	1·0	0·278	0·278	0·278	0·289	0·289	0·289	0·358	0·358	0·358
1·0	5·0	1·0	0·285	0·285	0·285	0·271	0·271	0·271	0·368	0·368	0·368
1·0	7·0	1·0	0·289	0·289	0·289	0·261	0·261	0·261	0·373	0·373	0·373
1·0	1·0	1·0	0·260	0·260	0·260	0·332	0·332	0·332	0·336	0·336	0·336
1·0	1·0	3·0	0·278	0·278	0·278	0·354	0·354	0·354	0·292	0·292	0·292
1·0	1·0	5·0	0·286	0·286	0·286	0·364	0·264	0·364	0·269	0·269	0·269
1·0	1·0	7·0	0·289	0·289	0·289	0·369	0·369	0·369	0·264	0·264	0·264

the mobilities of the ions is in the order: K$^+$>Na$^+$>Li$^+$.

Now the mobilities of an ion may be expected to be a function of solvation effects and those ions which partially destroy existing water structure in their immediate environment would be expected to have enhanced mobilities. This shows that the structure breaking order in these multicomponent solutions is: K$^+$> Na$^+$> Li$^+$.

This order holds good for a particular concentration range reported here and is not the same as determined at infinite dilution by conductance studies[11]. Such a behaviour has been observed earlier also[12].

An exactly parallel behaviour is observed in the system LiCl-NaCl-KCl-DMSO. The only difference being that the magnitude of the diffusion coefficient are comparatively much smaller at the same concentration. This is attributed to the lesser mobility of the ions in DMSO and this is actually observed through transference number measurements[13,14]. Another important feature is that the change in the diffusion coefficient with concentration is also very small.

The main diffusion coefficients, $(D_{ii})_0$, are considerably less than the diffusion coefficient in the binary systems. This suggests that in the presence of additional electrolytes the mobility of the ions is suppressed and the electroneutrality condition imposes more restraint on the ions representing the main diffusion coefficient and thus $(D_{ii})_0$ have the lesser value. The decrease in mobility has also been observed in conductance studies of multicomponent electrolyte solutions[11].

Acknowledgement

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