

CHAPTER VII

Solubility and Transfer Free Energy of 1:1 Electrolytes From Water to 2-Methoxyethanol and 1,2-Dimethoxyethane.

The knowledge of ion solvent interactions in non-aqueous media is of considerable fundamental and technological importance. Increased uses of non-aqueous solvents as reaction media both in inorganic and organic chemistry, and their importance in industry make their studies in these solvents imperative to have fundamental information on the thermodynamic properties of the electrolytes. In addition, thermodynamic data for these systems will give considerable insight into the structure of electrolytic solutions in general. An important parameter towards understanding of these interactions is the Gibbs transfer free energies of an ion from the reference solvent to the solvent in question, as it reflects the differences in the interaction of the ion with the solvent molecules.

As part of our programme towards understanding the ion-solvent interactions in 2-methoxyethanol (ME) and 1,2-dimethoxyethane (DME), the standard free energies of transfer, ΔG_t° , of several ions such as Li^+ , Na^+ , K^+ , Rb^+ , Cs^+ and halide ions (Cl^- , Br^- , I^-) have been determined using the extra-thermodynamic assumptions based on the reference electrolyte method¹.

Experimental

2-Methoxyethanol (G.R.E. Merck) and 1,2-dimethoxyethane (Fluka) were purified as described previously (Chapter II).

Alkali metal halides were of Fluka's purum or puriss grade, recrystallised from water and dried in vacuum for 2 days before use. Sodium tetraphenylborate (Puriss, Fluka) was recrystallised from acetone and dried in vacuo at 80°C for 72 hours. Tetraphenylphosphonium bromide (Fluka, Puriss) was dissolved in a 9:1 (v/v) acetone-2-propanol mixture, reprecipitated by the addition of an equal volume of benzene and vacuum dried at 100°C². Tetraphenylarsoniumchloride (Fluka, Pro-Analysis) was recrystallized from acetone³.

The solubilities of the salts were measured by using an Orion Model EA 920 Ion Analyzer to within \pm 0.1% accuracy. We have determined the concentration of Na⁺, Cl⁻, Br⁻ and I⁻ ions by using specific Orion ion electrode (Catalogue No. Na⁺ - 9712BN; Cl⁻ - 9417BN; Br⁻ - 9435 BN; I⁻ - 9453 BN). A double junction reference electrode (Catalogue No. : 9002 with the internal chamber filled with a saturated solution of AgCl and the outer chamber filled with a solution of 10% KNO₃) was used with each of the ion selective electrode. A thermostatic bath maintained at 25 \pm 0.1°C was used for our measurements. Saturated solutions were prepared by mild shaking of the salts containing a large excess of the solid in respective solvents for 3-4 hours and then equilibrated at 25°C. The solutions were shielded from light during equilibration. Every 2-3 days, portions of the solutions were withdrawn, filtered if

necessary, appropriately diluted with respective solvents as required and their concentrations were determined using the specific ion selective electrode. A solution was considered saturated when two successive analysis at 2-3 days intervals indicated no change in concentration. Usually one week of shaking was sufficient to achieve saturation.

Each ion selective electrode was tested for Nernstian response. In order to check the correctness of the data, known concentrations of the samples were measured by using ion selective electrodes and the results were compared. At least two trials were given for all the solutions which were under study.

Results

The average values of solubility of the alkali halides in ME and DME at 25^o C are given in Tables 1 and 2. The deviations from the average values are also listed.

The standard free energy of solvation for a solute on the molar scale was calculated from the relation

$$\Delta G_{\text{Soln.}}^{\circ} = -RT \ln K \quad \dots (1)$$

where K is the equilibrium constant for the reaction



upon introduction of the Debye-Huckel expression for the mean activity co-efficients for these solutions, one obtains⁴

$$\Delta G_{\text{Soln.}}^{\circ} = 2.303 RT \left[-\nu \log m - \log \left(\nu_+^{\nu_+} \nu_-^{\nu_-} + \nu \delta_D d_0^{1/2} m^{1/2} \right) \right] \dots (3)$$

where d_0 is the density of the solvent, δ_D is the Debye-Huckel limiting slope, ν is the number of ions, ν_+ and ν_- are the number of positive and negative ions, respectively, and the other symbols have their usual significance.

Equation (3) has been applied to the data to obtain standard free energies of solution and these are combined with the reported free energies of formation of the respective crystalline salts⁵ to obtain the corresponding standard free energies of formation for the alkali metal halides. The results of these calculations are also listed in Tables 1 and 2.

The transfer activity co-efficients $m \gamma_i$'s of the electrolytes previously called the "medium effect", are derived from the transfer free energy ΔG_t° , which is the difference between the standard free energy of solute in water G_w° , and that in non-aqueous solvent G_s° :

$$\Delta G_t^{\circ} = G_s^{\circ} - G_w^{\circ} = RT \ln m \gamma_i \dots (4)$$

The transfer activity co-efficients, expressed as $\log m \gamma_i$ have been calculated from the solubility products:

$$\log m \gamma_i = {}_s pK - {}_w pK = \frac{1}{2.303 RT} \left[{}_s \Delta G_{\text{soln.}}^{\circ} - {}_w \Delta G_{\text{soln.}}^{\circ} \right] \dots (5)$$

The transfer free energies and transfer activity co-efficients of the electrolytes have been given in Tables 3 and 4 respectively. The standard free energies of solution in water, $\Delta G_{\text{Soln.}}^{\circ}(\text{H}_2\text{O})$, was taken from literature^{3,6}.

To determine the single ion free energies of transfer from water to ME or DME, tetraphenylarsonium⁷⁻¹⁴ tetraphenylborate ($\text{Ph}_4\text{AsBPh}_4$) and tetraphenylphosphonium^{14,15} tetraphenylborate (Ph_4PBPh_4) have been chosen as the reference electrolytes. Literature also does not provide any data on the evaluation of single ion transfer energies in ME and DME media based on the reference electrolyte assumptions. ΔG_t° values of the reference electrolytes have been obtained from the following relationships¹²⁻¹⁴,

$$\Delta G_t^{\circ}(\text{Ph}_4\text{AsBPh}_4) = \Delta G_t^{\circ}(\text{Ph}_4\text{AsCl}) + \Delta G_t^{\circ}(\text{NaBPh}_4) - \Delta G_t^{\circ}(\text{NaCl}) \quad \dots (6a)$$

and

$$\Delta G_t^{\circ}(\text{Ph}_4\text{PBPh}_4) = \Delta G_t^{\circ}(\text{Ph}_4\text{PBr}) + \Delta G_t^{\circ}(\text{NaBPh}_4) - \Delta G_t^{\circ}(\text{NaBr}) \quad \dots (6b)$$

The ΔG_t° values of Ph_4AsCl , Ph_4PBr , NaBPh_4 , NaCl and NaBr have been obtained from the solubility measurements of the salts in these solvents at 25°C. Single ion free energies of transfer have been calculated with the aid of extrathermodynamic assumptions¹⁴.

$$\Delta G_t^\circ(\text{Ph}_4\text{As}^+) = \Delta G_t^\circ(\text{BPh}_4^-) = 1/2 \Delta G_t^\circ(\text{Ph}_4\text{AsBPh}_4) \quad \dots (7a)$$

and

$$\Delta G_t^\circ(\text{Ph}_4\text{P}^+) = \Delta G_t^\circ(\text{BPh}_4^-) = 1/2 \Delta G_t^\circ(\text{Ph}_4\text{PBPh}_4) \quad \dots (7b)$$

The single ion transfer values for other ions have been evaluated in the way described below.

$$\Delta G_t^\circ(\text{Cl}^-) = \Delta G_t^\circ(\text{Ph}_4\text{AsCl}) - \Delta G_t^\circ(\text{Ph}_4\text{As}^+)$$

and, $\Delta G_t^\circ(\text{M}^+) = \Delta G_t^\circ(\text{MCl}) - \Delta G_t^\circ(\text{Cl}^-)$

where M = Li, Na, K, Rb, Cs. $\Delta G_t^\circ(\text{Br}^-)$ and $\Delta G_t^\circ(\text{I}^-)$ were obtained from the corresponding sodium salts. Similarly, $\Delta G_t^\circ(\text{i})$ values have also been obtained using tetraphenylphosphoniumtetraphenylborate assumption,

$$\Delta G_t^\circ(\text{Br}^-) = \Delta G_t^\circ(\text{Ph}_4\text{PBr}) - \Delta G_t^\circ(\text{Ph}_4\text{P}^+)$$

and, $\Delta G_t^\circ(\text{M}^+) = \Delta G_t^\circ(\text{MBr}) - \Delta G_t^\circ(\text{Br}^-)$ where M^+ is the alkali metal cations.

Ph_4AsCl is almost insoluble in DME. The free energy transfer for single ions have been evaluated in this medium from Ph_4PBPh_4 in a similar way.

$$\Delta G_t^\circ(\text{Br}^-) = \Delta G_t^\circ(\text{Ph}_4\text{PBr}) - \Delta G_t^\circ(\text{Ph}_4\text{P}^+)$$

$$\Delta G_t^\circ(\text{Na}^+) = \Delta G_t^\circ(\text{NaBr}) - \Delta G_t^\circ(\text{Br}^-)$$

$$\Delta G_t^{\circ}(\text{I}^-) = \Delta G_t^{\circ}(\text{NaI}) - \Delta G_t^{\circ}(\text{Na}^+)$$

$$\Delta G_t^{\circ}(\text{M}^+) = \Delta G_t^{\circ}(\text{MI}) - \Delta G_t^{\circ}(\text{I}^-)$$

where M = Li, K, Rb and Cs.

The transfer free energy of ions (molar scale) in different solvents are given in Tables 5 and 6.

The results $\log m \gamma_{\pm}$ based on the $\text{Ph}_4\text{AsBPh}_4$ and Ph_4PBPh_4 assumptions in ME (Tables 5 and 6) differs somewhat, even though the magnitude remains the same. Such type of differences have also been observed previously^{12,16}.

Discussion

An examination of the solubilities of alkali-metal salts (Tables 1 and 2) shows that solubilities decrease with increase in cation size and generally increase with increase in the size of anions. Solubilities of salts in ME and DME are comparable, although smaller than the corresponding solubilities in water (except in case of bromides). For the halides solubilities are usually in the order $\text{I}^- > \text{Br}^- > \text{Cl}^-$. Generally salts are much less soluble in DME than in ME. The solubility of NaBPh_4 decreases in the order $\text{DME} > \text{ME} > \text{H}_2\text{O}$. It is also observed that Ph_4PBr is much less soluble in DME than that in water, although the solubility is much greater in ME than in water. Ph_4AsCl is much less soluble in ME than that in water, whereas in DME it is almost insoluble.

It is apparent that the dissolution of a salt in different solvent systems depends on the lattice energy of the salt as

well as on the polarity and dielectric constant of the solvent.

The free energy of solvation $\Delta G_{\text{Solv.}}^{\circ}$ of any salt is thermodynamically given by¹⁷

$$\Delta G_{\text{Soln.}}^{\circ} = \Delta G_{\text{Lattice}}^{\circ} + \Delta G_{\text{Solvation}}^{\circ} \quad \dots (8)$$

where $\Delta G_{\text{Soln.}}^{\circ}$ is the standard free energy of solution obtained from solubility measurements. The lattice energy $\Delta G_{\text{lattice}}^{\circ}$ (and is usually calculated using Born Haber cycle) is obtained from literature¹⁸. $\Delta G_{\text{Solv.}}^{\circ}$ is the solvation free energy and is the summation of the different energy terms due to solute-solvent interactions of varied nature. When an electrolyte goes into solution. Naturally the lattice energy which binds the pure substances together is excluded. It is natural to expect $\Delta G_{\text{soln.}}^{\circ}$ to depend on $\Delta G_{\text{solv.}}^{\circ}$ and the higher dielectric constant (i.e., lesser coulombic forces between ions) and hydrogen bonding capability of water make the $\Delta G_{\text{solv.}}^{\circ}$ much more negative in water and $\Delta G_{\text{solv.}}^{\circ}$ (-ve) (stabilization) is expected to be in the order -

Water > ME > DME which make the solubility in different solvents to increase in the order Water > ME > DME which is also the sequence of hydrogen-bonding capabilities of these solvents.

Standard free energies of transfer, $\Delta G_{\text{t}}^{\circ}$ of electrolytes from water to ME and DME (Table 3) show that the transfer process is unfavourable for most of the salts. However, probable hydrophobic interactions renders NaBPh_4 less soluble in water than

in non-aqueous solvent. The sequence of solubility of Ph_4PBr in different solvents, water $\langle \text{ME} \rangle$ DME cannot be properly explained. Salts containing large polarizable organic ions like Ph_4As^+ have been found to have smaller free energies of transfer compared to those for other electrolytes.

Transfer free energy changes of neutral electrolytes may give some idea regarding the solute-solvent interactions but meaningful correlation is only possible if we get the transfer free energy changes of simple ions which have the enormous potentialities in quantitative correlations between equilibrium constants, rate constants, ion-activity scales etc. But the division of transfer free energy changes is not possible by thermodynamic method. Various extrathermodynamic assumptions¹⁹⁻²³ are needed to get the transfer activity coefficients of ions and the 'reference electrolyte method' has been considered to be the best method for division. The method is based on the equal division of free energy transfer of tetraphenyl arsonium tetraphenyl borate or tetraphenyl phosphonium tetraphenyl borate to get single ion values which can be subsequently utilised for determining the single ion values of other ions using suitable electrolytes. The single ion values obtained in this way are listed in Tables 5 and 6.

Though it is difficult to obtain a suitable expression for single ion free energies in solution, but Latimer, Pitzer and Slansky²⁴ have shown that the modified Born equation

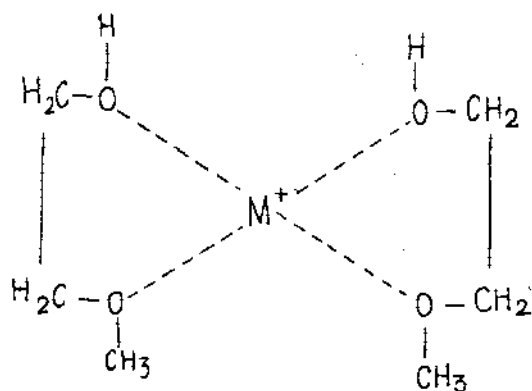
$$\Delta G_t^{\circ} = -e_1^2 \left[1 - \frac{1}{\epsilon} \right] / 2(r_1 + \delta) \quad \dots (9)$$

adequately expresses the free energy of hydration of the alkali metal and halide ions when δ for cations (δ_c) is 0.85 Å and δ for anions (δ_a) is 0.1 Å. The other symbols have their usual meaning. However, the equation (9) has been extended to derive free energy of solvation of ions in other solvents. In case of DMF, Criss et al⁴ observed that the best fit is obtained when $\delta_c = 0.85$ Å, $\delta_a = 1.00$ Å. We have also utilised these values to obtain the free energies of solvation of ions. The values are listed in Table 7. A plot of these ionic free energies of solvation vs. $1/(r_1 + \delta)$ is shown in Fig. (1). We have utilised the crystal radii given by Pauling²⁵.

Excellent correlations have been obtained when the solvent used is DME but deviations appear to be greater with ME as solvent. The deviations can be expected as the solubility of the alkali metal halides in ME are considerably high but the dielectric constant is low. Appreciable association can be expected in these cases. This is amply corroborated from the conductance²⁶ experiment, and the association constants (listed in tables 1 and 2) show that the association is appreciable. Therefore, proper corrections are necessary before we actually derive the single ion values.

The single ion free energy changes can be regarded to be the quantitative measure of ion solvent interactions. Though the structural variations can be better represented by ΔH° and $T\Delta S^\circ$ values, but they compensate each other to give simple free energy term ΔG° and in this chapter we are primarily concerned with the free energy of solvation of ions. Generally, a positive value of ΔG_t° indicates that the ions are more solvated in water (here the reference medium) than in ME or DME i.e., most of the cations Li^+ to Cs^+ are poorly solvated in ME or DME (Tables 5 and 6) but the transfer free energy of anions from water to ME or DME though positive but decreases with the increasing size of the anions i.e. the values of ΔG_t° are in the order $\text{Cl}^- > \text{Br}^- > \text{I}^-$. The large polarisable ions (BPh_4^- , Ph_4As^+ , Ph_4P^+ etc.) are poorly hydrated in water due to hydrophobic interactions and the solvation of these ions are found to be favoured in ME or DME relative to water (i.e., $\Delta G_{t(1)}^\circ = -ve$). The negative ΔG_t° values may also be due to cavity forming effect²⁷ generally associated with large sized ions. The sign, magnitude and order of $\Delta G_{t(1)}^\circ$ values for these ions indicate that their variations arise due to the combined effects of (i) increasing positive acid-base²⁸⁻³⁰ type interactions, (ii) Born type electrostatic interactions between the ions and solvent molecules and (iii) soft-soft interactions^{31, 32} superimposed on the above and acting in opposite direction. The observed

large positive values of ΔG_t° of Cl^- and Br^- ions in DME (Column 3, Table 6) indicate generally the dominant contribution of factors (i) and (ii). The relatively greater stabilization of I^- ion over the other halide ions may be attributed to its larger radius which render its softer as compared to Cl^- and Br^- ions. Also the observed reverse order of $\Delta G_t^\circ(\text{M}^+)$ with the radius of M^+ in ME is possibly due partly to the predominant contribution of Born-Type electrostatic interactions on the small sized cations and partly to the fact that due to possible steric hindrance the number of ME dipoles interacting with these small sized M^+ ions is much less than that in water. Alternatively, if one assumes that M^+ ion in ME is likely to be stabilized by the formation of electrostatically bound complex of the type $\text{M}(\text{ME})_2$ (I) similar to that proposed in DME³³, then the



observed order of $\Delta G_t^{\circ}(M^+)$ values is apparently the result of the combined effects of the Born-type electrostatic interactions and the predominantly large hydration of smaller cations. Thus the nature of ion-solvent interactions seems to be somewhat involved and is guided by the amalgamated effects of Born-type, acid-base and soft-soft interactions and/or of the structural changes of the solvents.

Table 1 : Solubility, Standard Free Energies of Solution and Standard Free Energies of Formation of Electrolytes in ME at 25°C

Salt	Solubility (molar)	$\Delta G_{\text{soln.}}^{\circ}$ (k Cal mol ⁻¹)	$-\Delta G_{\text{f}}^{\circ}$ (k cal mol ⁻¹)	$-\Delta G_{\text{solv.}}^{\circ}$ (k cal mol ⁻¹)	K_{A}° (dm ³ mol ⁻¹)
LiCl	$12.50 \pm 1.01 \times 10^{-1}$	-1.74	93.44	203.44	587.54 ± 42.66
NaCl	$4.82 \pm 0.62 \times 10^{-2}$	2.90	88.89	181.00	289.93 ± 31.97
KCl	$4.08 \pm 0.38 \times 10^{-2}$	3.14	94.45	165.16	409.95 ± 13.56
RbCl	$3.81 \pm 0.19 \times 10^{-2}$	3.23	93.57	159.57	762.32 ± 52.02
CsCl	$1.55 \pm 0.58 \times 10^{-1}$	1.27	95.33	155.93	973.42 ± 63.98
LiBr	$35.50 \pm 1.23 \times 10^{-1}$	-3.27	84.47	194.27	328.15 ± 25.08
NaBr	$4.90 \pm 0.86 \times 10^{-1}$	-0.38	83.48	175.88	127.34 ± 10.32
KBr	$1.20 \pm 0.13 \times 10^{-1}$	1.11	89.00	159.07	175.15 ± 8.86
RbBr	$1.725 \pm 0.09 \times 10^{-1}$	0.87	89.27	155.99	239.88 ± 16.59
CsBr	$2.05 \pm 0.07 \times 10^{-1}$	-3.21	90.73	150.33	524.58 ± 34.09

Contd. .

Table 1 (Contd..)

LiI	$34.00 \pm 1.19 \times 10^{-1}$	-3.18	67.21	181.61	_____
NaI	$33.50 \pm 1.14 \times 10^{-1}$	-1.89	59.88	167.98	_____
KI	$13.80 \pm 0.72 \times 10^{-1}$	-0.47	78.92	153.39	_____
RbI	$5.20 \pm 0.42 \times 10^{-1}$	2.88	78.27	148.37	_____
CsI	$4.90 \pm 0.17 \times 10^{-2}$	-1.29	76.82	140.82	_____
NaBPh ₄	$11.50 \pm 0.67 \times 10^{-1}$	-1.18	_____	_____	24.15 ± 0.90
Ph ₄ PBr	$8.50 \pm 0.51 \times 10^{-1}$	-2.15	_____	_____	_____
Ph ₄ ASCl	$17.00 \pm 0.81 \times 10^{-1}$				

^aRef. 26(b)

Table 2 : Solubility, Standard Free Energies of Solution and Standard Free Energies of Formation of Electrolytes in DME at 25°C

Salt	Solubility (molar)	$\Delta G_{\text{soln.}}^{\circ}$ (k cal mol ⁻¹)	$-\Delta G_{\text{f}}^{\circ}$ (k cal mol ⁻¹)	$-\Delta G_{\text{solv.}}^{\circ}$ (k cal mol ⁻¹)	K_{A} (dm ³ mol ⁻¹)
NaCl	5.45 ^a ± 1.72 × 10 ⁻⁷	17.07	74.72	166.83	
KCl	0.77 ^a ± 0.08 × 10 ⁻⁶	16.66	80.93	151.64	
RbCl	6.83 ^a ± 0.27 × 10 ⁻⁷	16.80	80.00	146.00	
LiBr	19.50 ± 0.89 × 10 ⁻¹	-3.11	84.31	194.11	
NaBr	8.90 ± 0.68 × 10 ⁻⁵	10.88	72.22	164.62	
KBr	5.50 ± 0.57 × 10 ⁻⁴	8.54	82.09	152.16	
RbBr	2.00 ± 0.17 × 10 ⁻⁵	12.73	77.65	144.37	
CsBr	6.50 ± 0.59 × 10 ⁻⁴	8.32	83.28	142.88	
LiI	6.20 ± 0.15 × 10 ⁻¹	-1.42	65.42	179.82	
NaI	16.50 ± 0.33 × 10 ⁻¹	-2.86	59.56	167.66	
KI	2.70 ± 0.88 × 10 ⁻²	3.15	73.88	148.35	

Contd..

Table 2 (Contd..)

RbI	$4.80 \pm 0.08 \times 10^{-2}$	2.32	75.48	145.58	
CsI	$1.20 \pm 0.43 \times 10^{-1}$	10.50	69.20	133.20	
NaBPh ₄	$13.50 \pm 1.09 \times 10^{-1}$	-2.56	-----	-----	18315.02 ^b
Ph ₄ PBr	$1.70 \pm 0.02 \times 10^{-3}$	7.03	-----	-----	

^aRef. 26(a)

^bRef. 26(c)

Table 3 : Free Energies of Transfer (ΔG_t°) of 1:1 Electrolytes From Water to Non-Aqueous Solvents at 25°C

Electrolytes	$\Delta G_{\text{soln.}}^\circ$ (H_2O) (k cal mol ⁻¹)	ΔG_t° (k cal mol ⁻¹)	
		ME	DME
LiCl	-9.90 ^a	8.16	—
NaCl	-2.15 ^a	5.05	19.22 ^b
KCl	-1.23 ^a	4.37	17.89 ^b
RbCl	-2.00 ^a	5.23	18.80 ^b
CsCl	-2.20 ^a	3.47	—
LiBr	-13.60 ^a	10.33	10.49
NaBr	-4.10 ^a	3.72	14.98
KBr	-1.41 ^a	3.04	9.95
RbBr	-1.64 ^a	2.75	14.37
CsBr	-0.38 ^a	1.25	8.70
LiI	-18.60 ^a	15.39	17.18
NaI	-6.54 ^a	3.36	3.68
KI	-2.79 ^a	0.90	5.94
RbI	-2.00 ^a	1.53	4.32
CsI	-0.10 ^a	2.98	10.60
NaBPh ₄	-0.21	-1.08	-2.35
Ph ₄ PBr	3.52	-4.70	3.51
Ph ₄ ASCl	-2.34	-0.19	—

^a Ref 6

^b Calculated from ref. 26(a)

Table 4 : Medium Effects of Electrolytes in ME and
DME at 25°C (molar scale)

Electrolytes	log $m\gamma$	
	ME	DME
LiCl	5.98	—
NaCl	3.70	14.09 ^a
KCl	3.20	13.12 ^a
RbCl	3.83	13.78 ^a
CsCl	2.54	—
LiBr	7.59	7.69
NaBr	2.73	10.98
KBr	2.23	7.29
RbBr	2.02	10.54
CsBr	0.92	6.38
LiI	11.28	12.59
NaI	2.46	2.69
KI	0.66	4.35
RbI	1.12	3.17
CsI	2.18	7.77
NaBPh ₄	-0.79	-1.72
Ph ₄ PBr	-3.45	2.57
Ph ₄ ASCl	-0.14	—

^a Calculated from ref. 26(a).

Table 5 , Free Energies for the Transfer of Single Ions
Based on $\text{Ph}_4\text{ASBPh}_4$ Assumption from Water to
2-Methoxyethanol at 25°C

Ion	r_c/R	$\Delta G_t^\circ/k \cdot \text{cal mol}^{-1}$	$\log m \gamma_i$
Li^+	0.60	5.19	3.80
Na^+	0.95	2.08	1.52
K^+	1.33	1.40	1.03
Rb^+	1.48	2.26	1.66
Cs^+	1.69	0.50	0.37
Cl^-	1.81	2.97	2.18
Br^-	1.95	1.64	1.20
I^-	2.16	1.28	0.94
Ph_4AS^+	4.20	-3.16	-2.32
BPh_4^-	4.20	-3.16	-2.32

Table 6 : Free Energies for the Transfer of Single Ions Based on $\text{Ph}_4\text{P}^+\text{BPh}_4^-$ Assumption From Water to Non-Aqueous Solvent at 25°C

Ion	$\Delta G_t^\circ / k \text{ cal mol}^{-1}$		$\log m_i$	
	ME	DME	ME	DME
Li^+	10.28	18.06(0.07)	7.54	13.24(0.05)
Na^+	3.67	4.56	2.69	3.34
K^+	2.99	6.82(-0.47)	2.19	5.00(-0.34)
Rb^+	2.70	5.20(3.95)	1.98	3.81(2.99)
Cs^+	1.20	11.48(-1.72)	0.88	8.42(-1.26)
Cl^-	1.38	14.66	1.01	10.75
Br^-	0.05	10.42	0.04	7.64
I^-	-0.31	-0.88	-0.23	-0.65
Ph_4P^+	-4.75	-6.91	-3.48	-5.07
BPh_4^-	-4.75	-6.91	-3.48	-5.07

Values in paranthesis were calculated from the relationship, $\Delta G_t^\circ(\text{M}^+) = \Delta G_t^\circ(\text{MBr}) - \Delta G_t^\circ(\text{Br}^-)$

Table 7 : Ionic Free Energies of Solvation in ME and DME.

Ion	$-\Delta G_{\text{solv.}}^{\circ} / \text{k Cal mol}^{-1}$	
	ME	DME
Li ⁺	107.72	98.58
Na ⁺	86.77	79.41
K ⁺	71.65	65.57
Rb ⁺	67.04	61.35
Cs ⁺	61.49	56.28
Cl ⁻	55.59	50.87
Br ⁻	52.95	48.46
I ⁻	49.43	45.24

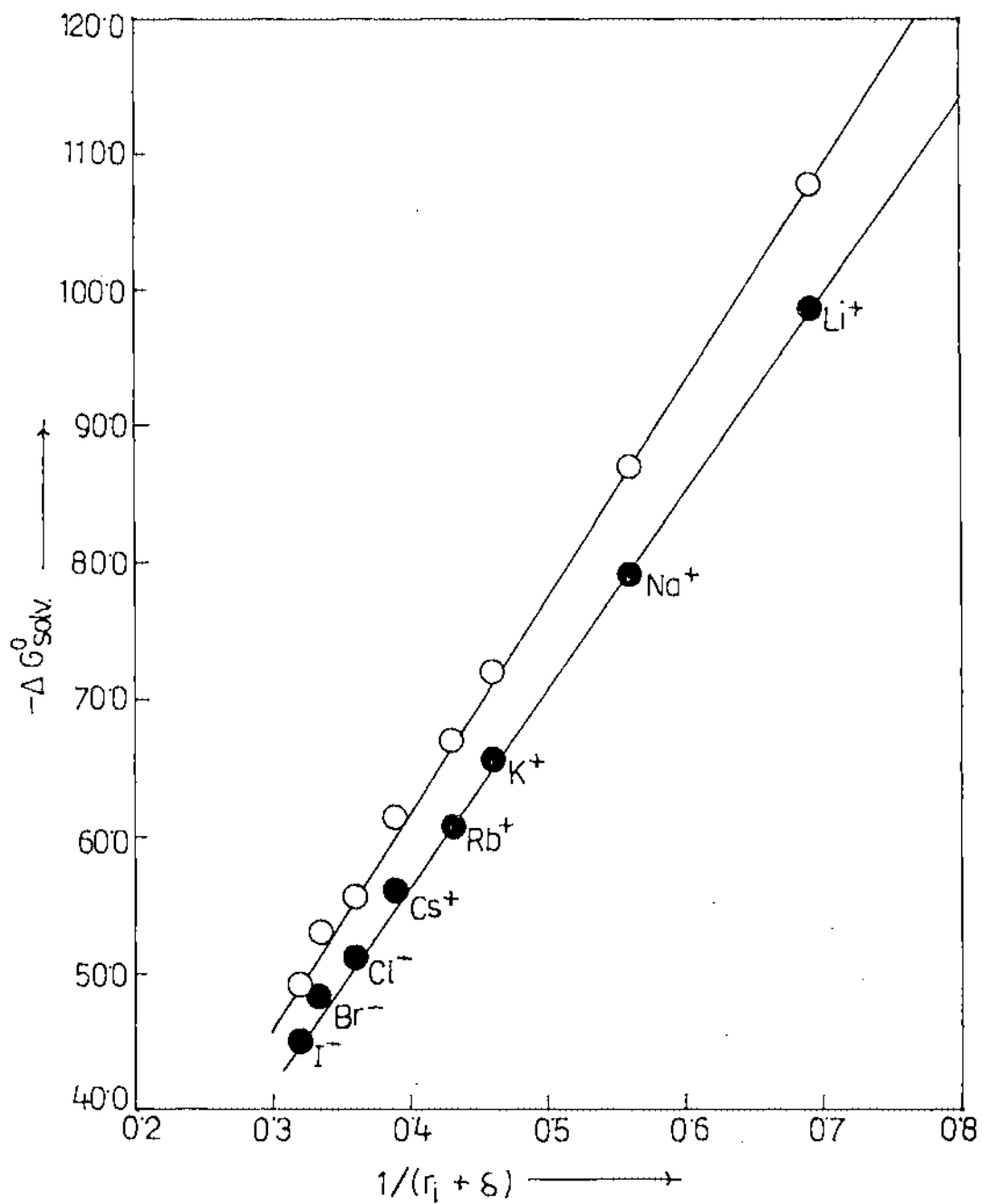


Fig. 1. - Plot of free energy of solvation of ions against their modified radii in ME,(O) & DME,(●).

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