

Transfer of ions between solvents: Some new results concerning volumes, heat capacities and other quantities

Yizhak Marcus

Department of Inorganic and Analytical Chemistry, The Hebrew University of Jerusalem, Jerusalem 91904, Israel

Abstract - Standard molar Gibbs free energies, enthalpies, and entropies of transfer between solvents have been reported by many authors for a large number of cations (mainly uni- and divalent) and anions (univalent). These quantities could be related to properties of the ions and the solvents, permitting predictions of such quantities. Also the transfer Gibbs free energies of divalent anions (sulfate and others) predicted on this basis agree with reported values. Only recently have the author and coworkers been able to extend this approach to the partial molar volumes and heat capacities of ions in various non-aqueous solvents using a multivariate statistical treatment, based, however, on a much more modest database. For these structure-related quantities the electrical properties of the solvents (permittivities, dipole moments) are not relevant, whereas their hydrogen bonding abilities are.

INTRODUCTION

The standard molar Gibbs free energies of transfer of electrolytes from some reference solvent (e.g., water (W), acetonitrile (MeCN), or N,N-dimethylformamide (DMF) into other, target, solvents, $\Delta_{tr}G^\circ$, have been measured by many authors. Solubility, liquid-liquid distribution, emf, and polarographic techniques have been mostly used for this purpose, and standard values are obtained by extrapolation to infinite dilution or explicit taking of activity coefficients into account. The contributions of the individual ions to $\Delta_{tr}G^\circ$ have been obtained from the measured data by the application of the additivity principle (the ions interact with the solvent independently of each other) and a suitable extrathermodynamic assumption. Of the assumptions that have been proposed (1) practically only the TATB and BBCr ones are being used nowadays. The TATB assumption (2,3) states that the contributions of its constituent - very similar - ions of opposite charge tetraphenylarsonium (TA) and tetraphenylborate (TB) to $\Delta_{tr}G^\circ$ are equal in all solvents. It has been used mainly for solubility, distribution and emf data, and yields values for anions as well as for cations. The BBCr assumption (4) states that the electrode potential of the bisbiphenylchromium(I)/(C couple is independent of the solvent. It has been applied to polarographic (voltammetric) data and provides values for cations only.

The standard molar enthalpy of transfer of ions, $\Delta_{tr}H^\circ$, is obtained from the calorimetric measurement of the heats of solution of electrolytes in the reference and target solvents. Standard values are obtained by extrapolation of such data to infinite dilution or corrections for heats of dilution. Individual ionic values are generally obtained by applying the TATB assumption (5). The enthalpy and entropy of transfer are related by $\Delta_{tr}H^\circ = \Delta_{tr}G^\circ + T \cdot \Delta_{tr}S^\circ$, so that the one is obtained if the other is known. The standard molar entropy of transfer of ions, $\Delta_{tr}S^\circ$, is obtained from the temperature coefficient of $\Delta_{tr}G^\circ$, mainly from dE°/dT or $dE_{1/2}/dT$ of emf and polarographic measurements or the use of thermocells (6). In the latter case the individual ionic contributions have been obtained from the assumption of a negligible thermal diffusion potential.

The values of $\Delta_{tr}G^\circ$, $\Delta_{tr}H^\circ$, and $\Delta_{tr}S^\circ$ obtained in this manner for individual ions and a large number of solvents have been interpreted qualitatively in terms of soft-soft or hard-hard interactions (7) as well as quantitatively (8,9) in terms of the detailed interactions that take place between an ion and the reference and the target solvents. Such detailed information can be obtained from the application of a multi-variate statistical regression program, where variables are permitted to enter the regression or are forced out from it on the basis of their contribution to the variance of a large database ($\Delta_{tr}G^\circ$ or $\Delta_{tr}H^\circ$ of many ions and solvents in this case) within certain statistical criteria. The variables tested are among a long list of potentially relevant ion and solvent properties: charge, size, polarizability, bonding ability, dipolarity, structuredness, etc.

The strong electrostatic interactions of the ions with the first solvation shell cancel out to a large extent on transfer (8), so that the ionic $\Delta_{tr}G^\circ$ are much smaller than the standard molar Gibbs free energies of solvation of the ions in the two solvents. More subtle interactions then become important, and if the reference solvent is water, it is expedient to consider small ions and large, hydrophobic ions separately. For the latter, the reciprocal of their radius, $1/r$, and their volume or molar refractivity, and the polarity/polarizability (the Kamlet-Taft π^*) and the cohesive energy density, δ^2 (for $\Delta_{tr}G^\circ$) or volume molar V (for $\Delta_{tr}H^\circ$) of the solvent are the properties needed. For small ions the properties required are z/r , z^2/r , r^3 , σ and R_D , where z is the algebraic charge, σ the softness parameter (10), and R_D the molar refractivity (Na D-line). The corresponding solvent properties are π^* , α (for anion transfer), β (for cation transfer), and V , where the Kamlet-Taft α is the ability to donate a hydrogen bond and the Kamlet-Taft β is the ability to donate an electron pair to form a coordinate bond, and for soft ions also μ , the solvent softness parameter (9) is important.

It is conspicuous that certain ion transfer functions have not till recently been considered adequately or at all on this or a similar basis. Lacking is a consideration of the standard molar Gibbs free energies of transfer of divalent anions between a reference and a target solvent (11). Nor have the standard partial molar volumes (12) and heat capacities (13) of ions in diverse solvents (or the corresponding quantities of transferred) been related to the properties of the ions and solvents. Such recent advances are summarized here.

TRANSFER OF DIVALENT ANIONS

There exist relatively few $\Delta_{tr}G^\circ$ values for divalent anions in the literature, and there is a good reason for this paucity. The $\Delta_{tr}G^\circ$ of divalent anions from water to most neat organic solvents are highly positive, i.e., unfavorable. Hence, any small contamination of the solvents with water would cause large errors. Data for mixed aqueous organic solvents must also be extrapolated to zero water content with caution: even if $\Delta_{tr}G^\circ$ is linear with the composition for a large fraction of its range, it may bend upwards near the end of the range. Another difficulty is the aptness of cations to ion-pair with divalent anions in solvents of only moderate relative permittivity ϵ , so that the obtaining of truly standard values by extrapolation to infinite dilution may not be reliable. These factors have been taken into account as best as can be, and a compilation of $\Delta_{tr}G^\circ$ values has been prepared (11) on the basis of mainly solubility data and the TATB (or the equivalent TPTB, where TP is tetraphenylphosphonium) assumption. The molal solubility m_s of uni-divalent salts (e.g., Ag_2SO_4) was transformed into standard molar Gibbs free energies of solution:

$$\Delta_{soln}G^\circ = -RT \ln(4 m_s^3 \gamma_{\pm}^3) \quad (1)$$

by the following expression for the mean molal activity coefficient in the saturated solution:

$$\ln \gamma_{\pm} = -2 A I^{1/2} / (1 + B I^{1/2}) \quad (2)$$

where $A = 1.8248 \times 10^6 (\epsilon T)^{-3/2}$ and $B = 1.5(\rho/\rho_w)^{1/2}(\epsilon_w/\epsilon)^{1/2}$, I is the (molal) ionic strength and ρ is the density of the solvent (subscript W pertaining to water). Then:

$$\Delta_{tr}G^\circ = \Delta_{\text{soln}}G^\circ - \Delta_{\text{soln}}G^\circ_w - RT \ln(\rho/\rho_w) \quad (3)$$

to convert to a molar (number density) basis.

The correlation expression for $\Delta_{tr}G^\circ$ with the properties of small (univalent) anions previously found (8) is:

$$\Delta_{tr}G^\circ = (3.02 \Delta\pi^* + 7.47\Delta\alpha - 0.0383\Delta V)z/r + 30.3\Delta\alpha \cdot \sigma - 11.7\Delta V \cdot r^3 + 0.29\Delta\pi^* \cdot R \quad (4)$$

where Δ denotes the difference of the property for the target and the reference solvents and r is in nm and V and R_D in $\text{cm}^3 \text{mol}^{-1}$. The applicability of this correlation to the data is shown in Table 1, in view of the expected reliability of the data, $\pm 10 \text{ kJ mol}^{-1}$. Where a range of calculated values is shown, this is due to the range of estimates of the softness parameter σ in eq. (4) for anions where no electron affinities are known.

Table 1. Comparison of experimental and calculated $\Delta_{tr}G^\circ/\text{kJ mol}^{-1}$ (mol dm^{-3} scale, TATB assumption) for transfer of divalent anions from solvent^a A to B at 298–303 K (from ref. 11).

Anion	A	B	$\Delta_{tr}G^\circ$ exptl.	$\Delta_{tr}G^\circ$ calcd.	Anion	A	B	$\Delta_{tr}G^\circ$ exptl.	$\Delta_{tr}G^\circ$ calcd.		
SO_4^{2-}	water	MeOH	36, 34, 30, 28, 57	34	SO_4^{2-}	MeOH	MeCN	53	55		
		EtOH	37, 99	46			NMF	-8	20		
		EG	53, 47, 27	37			DMF	18	71		
		DME	61	118			DMSO	52	68		
		THF	54	113			EtOH	MeCN	49	43	
		Diox	66, 59, 65, 133	114			Diox	MeCN	53	-25	
		Me ₂ CO	77, 194	103			DMSO	53	-12		
		MeCN	89, 81, 79, 13	89			EG	MeCN	54	52	
		NMF	47	54			DMSO	41	65		
		DMF	83	105			CO_3^{2-}	water	EG	5	53
		Py	149, 133	106			$\text{S}_2\text{O}_3^{2-}$	water	MeOH	85	25–27
		DMSO	115, 108, 98, 112, 131	102			$\text{Cr}_2\text{O}_7^{2-}$	water	Me ₂ CO	49	29–45
			PtCl_6^{2-}	water	MeOH	21	4–7				
				water	EtOH	21	4–9				

^a MeOH = methanol, EtOH = ethanol, EG = 1,2-ethanediol, DME = 1,2-dimethoxyethane, THF = tetrahydrofuran, Diox = 1,4-dioxane, Me₂CO = acetone, MeCN = acetonitrile, NMF = N-methylformamide, DMF = N,N-dimethylformamide, Py = pyridine, DMSO = dimethyl sulfoxide.

Some discrepancies are noted in Table 1 between the experimental and the calculated values that are beyond the ordinary experimental errors. Glaring cases are transfers to or from dioxane (and other ethers). Contamination by water and incomplete electrolytic dissociation are likely to have caused the unusually high solubility m_s of silver sulfate reported (14) for this solvent, that gives rise to the $\Delta_{tr}G^\circ$. The serious discrepancy noted for transfer from methanol to DMF cannot be explained, but that for transfer of thiosulfate is probably due to an incorrect estimate of the radius r used for the calculation according to eq. (4).

Taking eq. (4) to be valid for the divalent anions, it is seen that the dominant terms in $\Delta_{tr}G^\circ$ are the ones in $\Delta\alpha$, multiplied by z and by σ (for hard anions), both factors being negative. These terms make the transfer highly unfavorable. On the other hand, the pairs of terms in ΔV

and $\Delta\pi^*$ tend to oppose each other, so that their contribution is small. For a given solvent, the larger and softer the anion, the less positive is $\Delta_{tr}G^\circ$ but it is still unfavorable. The measured transfer of salts, however, depends on the cations as well as on the divalent anion, hence is often "heteroselective" (15), but a favorable transfer of a salt from water even to a mixed aqueous organic solvent is rarely found: transfer of silver sulfate into water-rich acetonitrile is such a case. Its solubility in this mixture is higher than in water, due to the strong preference of silver ions for the acetonitrile component and the not so strong aversion of the sulfate for it, when sufficient water is available to solvate it preferentially (15).

THE VOLUME CHANGE ON ION TRANSFER

The standard molar volume change of transfer, $\Delta_{tr}V^\circ$, is the difference between the standard partial molar volumes of the ion in the reference and the target solvents. The available database (12) for 298 K is limited to univalent ions: alkali metal, ammonium, halide, SCN^- , NO_3^- , and ClO_4^- among the small ions and tetraalkylammonium and the ions of TATB and TPTB among the large, hydrophobic ones. The list of target solvents comprises MeOH, EtOH, EG, NMF, PC, DMF, MeCN, MeNO₂, and DMSO (see the bottom of Table 1 for the abbreviations, also PC = propylene carbonate and MeNO₂ is nitromethane), the reference solvent being water. The TPTB assumption was used to split the electrolyte data into the ionic contributions, but the average difference of $\bar{V}^\circ(Ph_4P^+) - \bar{V}^\circ(BPh_4^-) = 2 \text{ cm}^3 \text{ mol}^{-1}$ for all solvents, based on the van der Waals volumes, was applied. The precision of the data (12) is estimated at $\pm 2 \text{ cm}^3 \text{ mol}^{-1}$.

The stepwise multivariate linear regression method mentioned in the introduction was applied to the database. The large ions showed the expected dependence on r^3 , i.e., the intrinsic volume of the ions, as the major ion property of importance. The rest of the variability was explained by the molar refraction R_D of the ions, differentiating between tetraalkyl and tetraphenyl ions. The resulting expression was:

$$\Delta_{tr}V^\circ = 0.146 \cdot r^3 [\Delta V - 7.1\Delta\alpha + 0.44\Delta\delta] - 0.055 \cdot R_D [\Delta V - 8.6\Delta\alpha] \quad (5)$$

where α is the polarizability of the solvent, the other symbols having been defined above. The difference in the molar volumes of water and the target solvent is seen to be the leading term of the solvent dependence, reflecting the packing of solvent molecules near the ions, but this is modified by the ability of the solvent to accommodate itself in tight places, its polarizability helping, its structuredness (measured by δ) impeding it. The dependence on the solvent properties that is noted shows these ions to be "solvated", contrary to the premise of Krungalz (16).

For the small ions the situation is more complicated, since the electrostriction of the solvent in the field of the ion requires to be taken into account. Thus Li^+ and Na^+ have negative \bar{V}° values in all solvents (except Na^+ in DMSO). For the volumes of transfer of these ions, again, their intrinsic volumes are of importance, but insufficient to account for most of the variability. A term in the ability of the ions to hydrogen bond to the solvents, HB (17), when added to the term in the volume, do account for 80 to 96% of the variability of $\Delta_{tr}V^\circ$. The resulting expression is:

$$\Delta_{tr}V^\circ = 0.08 \cdot r^3 [\Delta\delta + 0.20\Delta V] - 0.88 \cdot HB [\Delta\kappa_r - 0.9\Delta g] \quad (6)$$

where κ_r is the isothermal compressibility and g the Kirkwood dipole orientation parameter of the solvent, a measure of its structuredness (18). This expression could be used for the prediction of unavailable \bar{V}° values, e.g., for Rb^+ or F^- for several of the above named solvents and of these and other univalent ions in solvents, such as formamide, N-methylacetamide, acetone, and hexamethyl phosphoric triamide, where no TPTB data are known for splitting of electrolyte data into ionic values. The results are shown in Fig. 1.

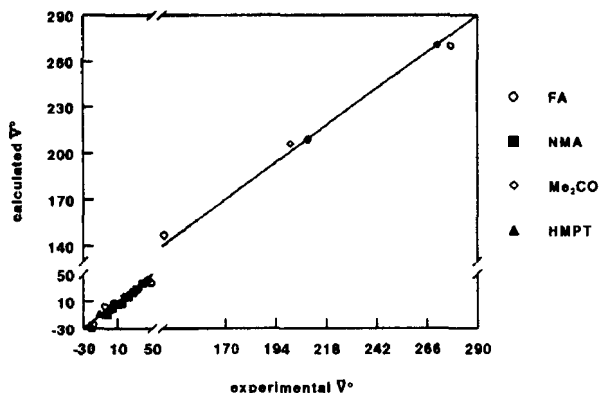


Fig. 1. Calculated vs. experimental \bar{V}° values in $\text{cm}^3 \text{mol}^{-1}$ in FA (formamide), NMA (N-methylacetamide), Me_2CO (acetone) and HMFT (hexamethyl phosphoric triamide). The straight line has a slope of unity.

The dependence of $\Delta_{\text{tr}}V^\circ$ of the small ions on the compressibility of the solvents, modified by their structuredness, as measured by g , i.e., their resistance to being restructured, is a good indication of the origin of this effect in the electrostriction caused by the field of the ion (19).

THE HEAT CAPACITY CHANGE ON ION TRANSFER

The standard molar change of heat capacity at constant pressure, $\Delta_{\text{tr}}C_p^\circ$, on the transfer of ions from a reference solvent to target solvents is the difference between the standard partial molar quantities in these solvents (13). Data from the literature for 298 K, mainly obtained by flow microcalorimetry, partly from temperature coefficients of heats of solution, formed the database submitted to the statistical evaluation described above. The TPTB assumption has again been invoked, due to the similarity of the values (20) of $C_p^\circ(\text{TP},g)$ and $C_p^\circ(\text{TB},g)$: 366.26 and 363.68 $\text{J K}^{-1} \text{mol}^{-1}$, the difference being small compared with the expected uncertainty of the data, $\pm 20 \text{ J K}^{-1} \text{mol}^{-1}$. As for the volumes, a separate treatment of the large, hydrophobic ions and the small ions is expedient.

For the tetraalkylammonium ions, the only relevant variable describing ion properties is the number of carbon atoms, n_c . For transfer from water the linear expression:

$$\Delta_{\text{tr}}C_p^\circ = a + b \cdot n_c \quad (7)$$

holds, where for transfer into protic solvents: MeOH, EtOH, and $n\text{PrOH}$ (1-propanol) $a = 225$ and $b = -54.9$ whereas for transfer into aprotic solvents: DMF, MeCN, and PC $a = 287$ and $b = -64.2$. The $C_p^\circ(\text{R}_4\text{N}^+,g)$ values also depend linearly on n_c : $a = 7$ and $b = 23.0$. The dependence of the coefficients in eq. (7) on solvent protic/aprotic class (not individual members) shows that there is some ion solvent interaction, i.e., the ions are "solvated", again contrary to Krumgalz's premise (16). The molar difference in the heat capacity of solvation of a CH_2 group for alcohols vs. water is $b/4 = -13.7$ and for the aprotic solvents it is $b/4 = -16.1 \text{ J K}^{-1} \text{mol}^{-1}$, these large values signifying the collapse of the quasi-clathrate water structure around the hydrophobic chains on transfer. The positive intercepts, a , reflect the behavior of the hypothetical " $\text{N}(\text{H}_4)^+$ " ion, which has negligible size and differs from the actual ammonium ion, NH_4^+ . The former, hypothetical ion orients water strongly, preventing it from absorbing energy that would allow librations and rotations, so that transfer to less strongly held more bulky solvents is accompanied by a large increase in heat capacity.

The heat capacity of transfer of small ions from water into aprotic solvents is given by:

$$\Delta_{\text{tr}}C_p^\circ = [-0.45\Delta\delta - 19\Delta\beta]z + [3.5\Delta\delta - 170\Delta\beta]/r + [-0.08\Delta\delta + 7.1\Delta\beta]R_b \quad (8)$$

For transfer into protic solvents, however, the expression:

$$\Delta_{\text{tr}}C_p^\circ = [-1.8\Delta\delta + 15\Delta\kappa_r]z + [0.11\Delta\delta - 6.1\Delta\kappa_r]/r + [-0.48\Delta\delta + a \cdot \text{HB}]R_b \quad (9)$$

is to be used, with $a \cdot \text{HB}$ taking the value $15.5 \cdot \Delta\beta$ for cations and $11.9 \cdot \Delta\alpha$

for anions. (Note that HB here pertains to the solvent, not the ion properties to enter into hydrogen bonding according to the Kamlet-Taft scale (8)). For a given solvent, the term in z in both eq. (8) and (9) becomes of opposite signs for cations and anions. The ability of these expressions to fit the data is shown in Fig. 2, with the linear correlation having a slope of 0.79 instead of the expected 1.00, meaning that a sizable fraction of the variability of the data could not be explained.

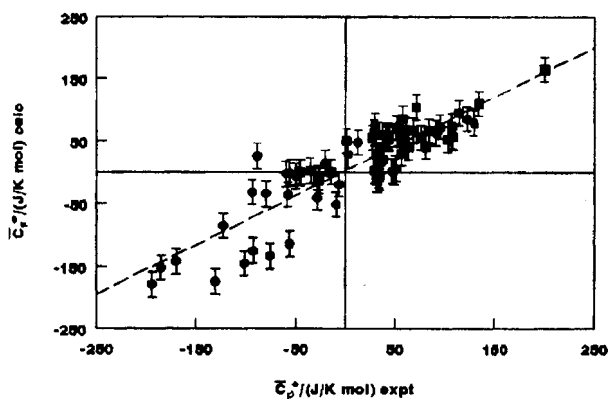


Fig. 2. The calculated vs. the experimental standard partial molar heat capacities of small ions in non-aqueous solvents. Squares pertain to aprotic solvents and circles to protic ones.

The expressions do not permit the ready separation of the dependence on the ion and solvent properties and their relative contributions to the observed quantities. Good donor solvents have lower \bar{C}_p^0 (even negative) values for cations than poorer donor solvents, corresponding to the structure-making ability of small cations in water. The term in the molar refraction (polarizability) is larger for anions than for cations, providing for positive \bar{C}_p^0 values. Loosening of solvent structure by ions, permitting more energy to be absorbed, accounts for the term in $\Delta\delta$ and the opposing term in $\Delta\kappa_T$. The importance of the solvent Lewis basicity (β) for cations and Lewis acidity (α) for anions relates to the types of interactions that take place (13).

REFERENCES

1. Y. Marcus, *Pure Appl. Chem.* **58**, 1721-1736 (1986).
2. E. Grunwald, G. Baughman, and G. Kohnstam, *J. Am. Chem. Soc.* **82**, 5801 (1960).
3. R. Alexander and A.J. Parker, *J. Am. Chem. Soc.* **89**, 5549 (1967).
4. G. Gritzner, *Inorg. Chim. Acta* **24**, 5 (1977).
5. C.V. Krishnan and H.L. Friedman, *J. Phys. Chem.* **73**, 3934 (1969).
6. G. Gritzner and A. Lewandowski, *J. Chem. Soc., Faraday Trans.* **87**, 2599 (1991).
7. G. Gritzner, *Z. Phys. Chem. (Munich)* **156**, 99 (1989).
8. Y. Marcus, M.J. Kamlet, and R.W. Taft, *J. Phys. Chem.*, **92**, 3613 (1988).
9. Y. Marcus, *J. Phys. Chem.* **91**, 4422 (1987).
10. Y. Marcus, *Thermochim. Acta* **104**, 389 (1986).
11. Y. Marcus, *Z. Naturforsch.* **50a**, 51 (1995).
12. Y. Marcus, G. Hefter, and T.-S. Pang, *J. Chem. Soc., Faraday Trans.* **90**, 1899 (1994).
13. Y. Marcus and G. Hefter, unpublished results, 1995.
14. G. Rajendran and C. Kalidas, *J. Chem. Eng. Data* **31**, 226 (1986).
15. H. Strelow and H. Schneider, *Pure Appl. Chem.* **25**, 327 (1971).
16. B.S. Krungalz, *J. Chem. Soc., Faraday Trans.* **1** **79**, 571 (1983).
17. Y. Marcus, *J. Phys. Chem.* **95**, 8886 (1991).
18. Y. Marcus, *J. Solution Chemistry* **21**, 1216 (1992).
19. S.D. Hamann and S.C. Lim, *Aust. J. Chem.* **7**, 329 (1954).
20. A. Loewenschuss and Y. Marcus, *J. Phys. Chem. Reference Data*, **16**, 61 (1987).