SOME REGULARITIES IN THE FREE ENTHALPIES
OF TRANSFER OF UNIVALENT IONS FROM WATER
TO ORGANIC POLAR SOLVENTS

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Employing recent data from the literature and our results for the system water–nitrobenzene, the quantity $\Delta°G_i^{tr}$ has been found to be in a simple relation to the free enthalpy of hydration for ions with electronic structures of rare gases and for ClO_4^-. This relation, *viz.* $\Delta°G_i^{tr} = a - b\Delta°G_{hydr}$, is compared with Born's modified equation. The parameter a is probably a measure of the non-electrostatic effect in the transfer of ions and appears to be closely related to the structure of the solvent.

The free enthalpy of transfer $(\Delta°G^{tr})$ is a fundamental thermodynamic quantity determining the affinity of an electrolyte to a given solvent compared to a reference solvent (usually water). Although great progress has been made in recent years in the study of non-aqueous solutions of electrolytes and interpretation of experimental data (*e.g.* the conception of "reference electrolytes" for determining the individual values of $\Delta°G_i^{tr}$, refs[1,2], *cf.* also[3−5]), some general rules describing the value of $\Delta°G_i^{tr}$ have not yet been revealed.

The present paper deals with the values of $\Delta°G_i^{tr}$ in relation to the free enthalpies of hydration, $\Delta°G_i^{hydr}$, of the corresponding ions. Employing this new approach to the problem we tried to interpret the values of $\Delta°G_i^{tr}$ for the equilibrium system water–nitrobenzene. A more detailed investigation of the literature data has revealed that the criterion employed has a more general applicability.

RESULTS AND DISCUSSION

The free enthalpy of transfer, $\Delta°G_i^{tr}$, will express the difference between the free enthalpy of solvation of an ion i in the organic solvent, $\Delta°G_i^{solv}$, and the free enthalpy of hydration of this ion, $\Delta°G_i^{hydr}$. The values of $\Delta°G_i^{tr}$ can be determined on the basis of some non-thermodynamic assumption[1,2] from the values of the sums $\Delta°G_{Me^+}^{tr} + \Delta°G_{A^-}^{tr}$ for the electrolyte Me^+A^- as a whole. These values are experimentally accessible[3].

Owing to the complexity of the process of ionic solvation it is generally impossible to predict to what extent the ion i will be solvated in a polar organic solvent if its free enthalpy of hydration is the only known value. Nevertheless, it can be assumed that in the case of small ions with electronic configurations of rare gases, where the specific interaction with the solvent is absent, the quantity $\Delta°G^{solv}$ will be a function of $\Delta°G^{hydr}$. Then $\Delta°G^{tr} = \Delta°G^{solv} - \Delta°G^{hydr}$ must also be some function of $\Delta°G^{hydr}$. To verify the correctness of this assumption the values of $\Delta°G_i^{tr}$ from refs.[6,7] and other communications were plotted vs. $\Delta°G_i^{hydr}$ (Figs 1 and 2).

The values of $\Delta°G^{hydr}$, taken from Mischenko and Poltorackij's monograph[13], are based on the assumption $\Delta°H_{Cs^+}^{hydr} = \Delta°H_{I^-}^{hydr}(\Delta°H_{H^+}^{hydr} = -265$ kcal/mol). In the literature (e.g.[14]) the values of $\Delta°G^{hydr}$ have been obtained with the aid of other assumptions but the differences
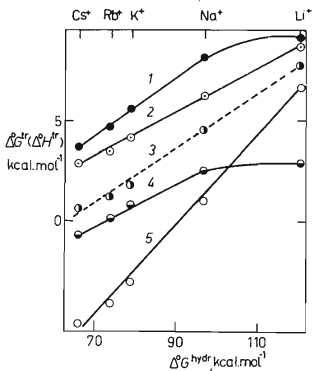

Fig. 1

Free Enthalpies of Transfer of Alkali Cations as Functions of their Free Enthalpies of Hydration

The points of curves $1-3$ are considered by respective authors to be closely corresponding to the absolute values of $\Delta°G^{tr}$. The values of $\Delta°G^{hydr}$ were taken from[13]. The dashed curves represent the courses of $\Delta°H^{tr}$. Some of the curves in Figs 1 and 2 are shifted vertically for greater clarity. From the values taken from these figures the below indicated amount of kcal. mol^{-1} should be substracted. 1 System water–nitrobenzene, extraction system; the values were calculated from extraction data employing the "Ph$_4$AsBPh$_4$ assumption"[6]. 2 Water–acetonitrile; the data were obtained from half-wave potentials and the distribution of values according to Born's modified equation[8]. 3 Water–propylene carbonate, ($\Delta°H_i^{tr}$, -7 kcal mol^{-1}); the data were obtained by measurement of heats of solution employing the "Ph$_4$AsBPh$_4$-assumption"[9]. 4 Water–nitromethane, extraction system, relative values from extraction measurements[5]. 5 Water–nitromethane[5].

between $\Delta°G_i^{hydr}$ for cations and anions are practically the same. Consequently, the selection of other fundamental values would only shift the curves in Figs 1 and 2 along the axis of abscissae, but the shapes of the curves would not be significantly altered. In this connection it should be pointed out that the spread of the values of $\Delta°G_i^{tr}$ reported by different authors is considerable in some cases, as described *e.g.* for the system water–methanol[3]. We have not selected the "best" values, but employed some of the latest data. We believe that further refinement of some of these data will not markedly change the overall character of the curves in Figs 1 and 2.

From Figs 1 and 2 it is evident that in most cases the dependence of $\Delta°G_i^{tr}$ on $\Delta°G_i^{hydr}$ can be expressed in the form

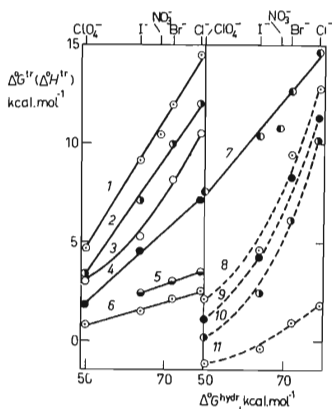$$\Delta°G_i^{tr} = a - b \cdot \Delta°G_i^{hydr} \qquad (1)$$

FIG. 2

Free Enthalpies of Transfer of Halide Anions and ClO_4^- as Functions of their Free Enthalpies of Hydration

The points of all curves are considered by the respective authors to be closely corresponding to the absolute values of $\Delta°G_i^{tr}$ or $\Delta°H_i^{tr}$. The values of $\Delta°H_i^{tr}$ are expressed by dashed curves. *1* System 50% (w/w) dioxan +50% water, the "Ph$_4$AsBPh$_4$ assumption"[10]. *2* Water–dimethylformamide, ($\Delta°G_i^{tr}$, $-$ 3 kcal mol^{-1}), data of solubilities[11]. *3* Water–dimethylsulphoxide ($\Delta°G_i^{tr}$, $-$ 2·5 kcal mol^{-1}) (ref.[11]). *4* Water–nitrobenzene, extraction system[6]. *5* Water–formamide[11]. *6* Water–methanol[11]. *7* Water–acetonitrile, calculated from half-wave potentials, ($\Delta°G_i^{tr}$, $-$ 9 kcal mol^{-1}) (ref.[8]). *8* Water–dimethylformamide, ($\Delta°H_i^{tr}$, $-$ 10 kcal mol^{-1}) (ref.[12]). *9* Water–propylene carbonate, ($\Delta°H_i^{tr}$, $-$ 5 kcal mol^1) (ref.[9]). *10* Water–dimethylsulphoxide, ($\Delta°H_i^{tr}$, $-$ 5 kcal mol^{-1}) (ref.[12]). *11* Water–methanol, (ref.[12]).

with different parameters, a and b, for the cations and the anions (see Table I, aceto-nitrile). The behaviour of the ion ClO_4^- very well fits the curves for ions with electronic configurations of rare gases. The dependence of $\Delta^\circ H_i^{tr}$ on $\Delta^\circ G_i^{hydr}$ for alkali cations is linear (curve 3 in Fig. 1), but in the case of anions the values of $\Delta^\circ H_i^{tr}$ at low values of $\Delta^\circ G_i^{hydr}$ are relatively higher. This curvature is natural if we consider the different courses of the functions $\Delta^\circ H_i^{tr}$ and $\Delta^\circ G_i^{tr}$ for bulky ions[15]. In the case of alkali cations transferred into solvents where they are more solvated than in water (dimethylformamide, dimethylsulphoxide) the spread of the relative values of $\Delta^\circ G^{tr}$ (calculated from half-wave potentials[16]) is greater and it is impossible to draw straight lines through them. It is noteworthy, however, that with the cations Cs^+, Rb^+, K^+ and Na^+ the values of $\Delta^\circ G^{tr}$ are little different (at most by 1 kcal mol^{-1}), which deviation, despite the possible experimental inaccuracy, is much smaller than that observed on the plots in Fig. 1. A probable explanation of this fact will be dealt with below.

The parameters a and b (in some cases only the parameter b was known, unless the values of $\Delta^\circ G^{tr}$ were divided into the ionic contributions) of the straight lines in Figs 1 and 2 are given in Table I.

Before equation (1) is discussed more in detail it will be shown that the found straight lines are in accordance with Born's modified equation (2), which at present is the one most frequently used to discuss the determined values of $\Delta^\circ G_i^{tr}$. According

TABLE I
The Constants of Equation (1)

Solvent	Cations		Anions	
	a, kcal mol^{-1}	b	a, kcal mol^{-1}	b
Nitromethane $(H_2O)^a$	—	0·105	—	—
Acetonitrile	−4·75	0·112	−15·0	0·260
Nitrobenzene $(H_2O)^a$	−6·08	0·146	−9·75	0·236
Nitromethane	—	0·227	—	—
Methanol	—	—	−2·12	0·058
Formamide	—	—	−2·18	0·072
Dimethylformamide	—	—	−15·0	0·305
50% Dioxan–50% Water	—	—	−13·3	0·352

^{a} Extraction systems water–nitromethane and water–nitrobenzene. The value of a depends on the mode of distribution of the total $\Delta^\circ G^{tr}$ into the individual ion contributions and implies the assumption that $\Delta^\circ H_{Cs^+}^{hydr} = \Delta^\circ H_{I^-}^{hydr}$ (see[13]).

to Strehlow[3] and other authors[5] it applies

$$\Delta^\circ G_i^{tr} = \frac{Ne^2}{2(r_i + \delta_{H_2O})}\left(1 - 1/\varepsilon_{H_2O}\right) - \frac{Ne^2}{2(r_i + \delta_S)}\left(1 - 1/\varepsilon_S\right), \qquad (2)$$

where N and e have the usual meanings[3], r_i designates the crystallographic radius of an ion i, ε_S the relative permittivity of the solvent and δ_{H_2O}, δ_S are the corrective increments. Equation (2) is an empirical relation derived from Latimer, Pitzer and Slánský's finding[17] that the values of $-\Delta^\circ G_i^{hydr}$ of alkali cations and halide anions can be expressed by the first term on the right-hand side of equation (2). It is assumed that all the simplifications implied in equation (2) (neglect of ion-dipole and other electrostatic interactions, of the decrease of the dielectric constant near an ion, etc.) are compensated for by an appropriate choice of the parameter δ_S (δ_{H_2O} is a constant determined independently by confronting Latimer's equation with "experimental" $\Delta^\circ G_i^{hydr}$, but the same idea is applicable to this increment[3]). On the other hand it is known, however, that the relative permittivity of a solvent is often a rough and unsafe criterion of its solvation properties[16], so that the agreement of equation (2) with experiment may be accidental only.

Fig. 3 gives the "theoretical" curves calculated from equation (2) for alkali cations transferred from water to a solvent of relative permittivity $\varepsilon_S = 38$. Pauling's crystallographic radii[18] have been employed and a value of $\delta_{H_2O} = 0.75$ Å, which gave the best agreement with Mischenko's values of $\Delta^\circ G_i^{hydr}$. The family of curves in Fig. 3 exhibits one characteristic feature: the ratio of differences of $\Delta^\circ G_i^{tr}$, e.g. $(\Delta^\circ G_{Rb^+}^{tr} - \Delta^\circ G_{Cs^+}^{tr})$: : $(\Delta^\circ G_{Na^+}^{tr} - \Delta^\circ G_{K^+}^{tr})$, is approximately constant throughout the range of δ_S, the greatest difference being for the pair Li^+–Na^+, a smaller one for Na^+–K^+, and much smaller one for K^+–Rb^+ and Rb^+–Cs^+. This, of course, is only another expression of the fact that the plots of $\Delta^\circ G_i^{tr}$ vs. $\Delta^\circ G_i^{hydr}$ give straight lines of different slopes (cf. Figs 1 and 3). The greater differences in the values of $\Delta^\circ G_i^{tr}$, e.g. for Na^+ and Li^+, are a consequence of greater differences in $\Delta^\circ G_i^{hydr}$. The effect of ε_S in equation (2) on the final result is obliterated by the effect of δ_S, since the term $1 - 1/\varepsilon_S$ for ordinary polar organic solvents equals 0.97 to 0.99, whereas δ_S is roughly comparable (by the order of magnitude) with r_i. To conclude it can be said that a successful application of Born's modified equation to systems water–organic polar solvent essentially consists in good correlation of equation (1) with a polynomial $A/(r_i + \delta_{H_2O}) - A/(r_i + \delta_S)$.

The simplicity of the relation $\Delta^\circ G_i^{tr} = a - b \, \Delta^\circ G^{hydr}$ is rather surprising at first sight. Recently, however, it has been shown by Criss, Held and Luksha[19] that an analogous linear relation applies to the ion entropies ($\bar{S}_2^0 = kS_{str} + C$, where S_{str} is the part of the entropy associated with the intrinsic order of the solvent and C is a constant for the given ion). Equation (1) can also be rewritten into the form $\Delta^\circ G_i^{solv} = = a + (1 - b) \, \Delta^\circ G_i^{hydr}$, corresponding directly to Criss's equation $\bar{S}_2^0(S) = a +$

$+ b\bar{S}_2^0(H_2O)$, ref.[19]. Both equations are simple correlations of the thermodynamic quantities in organic solvents and in water. With the use of equation (1) it could be possible to verify the correctness of experimental data and some results become easier to understand. Thus in paper[8] the high affinity of ClO_4^- towards acetonitrile is considered difficult to explain, but from curve 7 in Fig. 2 it can be seen that the behaviour of this ion well accords with the general trend of the plots of $\Delta°G_i^{tr}$ vs. $\Delta°G^{hydr}$. The bents on curves 1 and 4 in Fig. 1 indicate a certain anomaly in the transfer of the Li^+ ion into water-saturated nitromethane and nitrobenzene. Incidentally, it has been proved that Li^+ ion enters the organic phase (nitrobenzene) as a hydrate, whereas K^+, Rb^+ and Cs^+ are not hydrated in aqueous nitrobenzene[20].

From the free enthalpy of transfer the so-called non-electrostatic term $(\Delta°G_n^{tr})$[21,22] is sometimes separated. For it is known that atoms of the rare gases (i.e. neutral particles corresponding by size[21] or electronic structure[5] to elementary ions) get also distributed in a definite manner between water and the organic phase. Although the definition of the non-electrostatic effect is somewhat obscure (different orientations of the solvent molecules around an ion and around the corresponding neutral particle and different polarisabilities of the two species[22]) semiquantitative correlation has been achieved for bulky organic ions between their distribution in the system water–organic solvent and the distribution of the corresponding neutral particles[10]. In the case of small inorganic ions, however, judging from the distribution of atoms of the rare gases, the correlation of their $\Delta°G_n^{tr}$ will probably be worse.
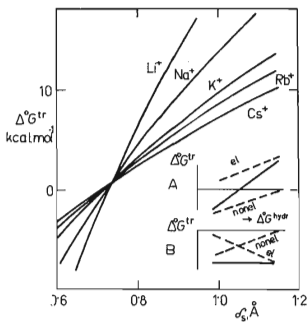

Fig. 3

$\Delta°G_i^{tr}$ of Alkali Cations for Transfer from Water into a Solvent of Relative Permittivity $\varepsilon_S = 38$ (calculated from Born's modified equation).

For details see the text.

In view of the linearity of the plots of $\Delta°G^{tr}$ vs. $\Delta°G^{hydr}$ for elementary inorganic ions it is to be expected that the plots of $\Delta°G_n^{tr}$ vs. $\Delta°G^{hydr}$ will also be roughly linear for these ions (it is hardly probable that the sum of two markedly non-linear functions $\Delta°G_e^{tr}$ and $\Delta°G_n^{tr}$, should take linear courses in all cases). If the assignment of $\Delta°G_e^{tr}$ is based on the identity of electronic structures of the ion and atom of a rare gas[5], then to the ions Na^+ and F^- is assigned the distribution of Ne, *etc.* The solubility of the rare gases in water and in 7 organic solvents has been found by Friedman[23] to obey the linear relation $\log x = a + bg$, where x is the mol fraction of the dissolved gas at 25°C and g is an empirical parameter. The free enthalpies of transfer, $\Delta°G_n^{tr}$, are then also linear in these coordinates. The differences between the values of g for the pairs Ne–A, A–Kr and Kr–Xe are in the ratio $1\cdot61 : 0\cdot88 : 1\cdot00$, whereas the ratio of differences in $\Delta°G^{hydr}$ is $3\cdot50 : 0\cdot88 : 1\cdot00$ for the anions F^-, Cl^-, Br^- and I^-, and $2\cdot25 : 0\cdot62 : 1\cdot00$ for the cations Na^+, K^+, Rb^+ and Cs^+, respectively[13]. Comparison of these values reveals that $\Delta°G_n^{tr}$ is indeed in a linear relation to $\Delta°G^{hydr}$ for the anions Cl^-, Br^- and I^-, whereas in the case of cations the agreement is not so good. Calculation for the system water–nitrobenzene (based on the solubilities of the rare gases in water[24] and in nitrobenzene[25]) gives approximately linear courses of $\Delta°G_e^{tr}$, the parameters being $a' = -1\cdot49$ kcal mol^{-1} and $b' = 0\cdot0989$ for the cations, and $a' = -0\cdot65$ kcal mol^{-1} and $b' = 0\cdot106$ for the anions. By comparison with the parameters given in Table I it appears that both the slope and the absolute value of a are lower on subtracting the non-electrostatic effect. A comparable decrease would be observed if the size of the ion were taken as a criterion of the value of $\Delta°G_n^{tr}$ (ref.[21]). Hence it seems likely that the moderate slope of the function $\Delta°G^{tr}$ vs. $\Delta°G^{hydr}$ for the cations in their transfer into solvents solvating them better than water does can very well be explained by the assumption of a relative increase of the slope, b, by the non-electrostatic effect (see Fig. 3; its right lower part illustrates transfer of cations from water into solvents where the electrostatic solvation is lower (A) and *vice versa* (B). The non-electrostatic term always increases the transfer into the organic phase).

Since $\lim\limits_{\Delta°G\to 0 hydr} \Delta°G_e^{tr} = 0$ the value of a should be a rough measure of the non-electrostatic interaction of a solvent. This seems to be true because the value of a approaches zero in the order of parameters of the so-called intrinsic order[19] of organic solvents, *i.e.* in the series dimethylformamide $\ll$ methanol $\leqq$ formamide[19]. The tabulated values of a are invariably negative because of all the solvents compared the intrinsic order of water is the highest. It is of interest that the quantity a has a high negative value for the transfer from water to the system 50% (w/w) water–50% dioxan, which suggests that the structure of water is strongly upset by the addition of this solvent. This conclusion is in keeping with reported data[26]. In one case the value of a would be expected to be positive, *viz.* in the transfer from H_2O to D_2O, since the intrinsic order of D_2O is higher than that of water[19]. In view of the low accuracy of the report-

ed values of $\Delta^\circ G_i^{tr}$ we preferred the use of the recently reported[27] value of $\Delta^\circ H^{tr}$. With the cations Na^+, K^+, Rb^+ and Cs^+ and with the halide anions the dependence of $\Delta^\circ H^{tr}$ on $\Delta^\circ G^{hydr}$ is indeed linear in all cases, the value of a being $+0.702$ and $+1.505$ kcal mol^{-1} for the cations and the anions, respectively. All these facts indicate that the structure of a solvent is one of the important factors governing the course of $\Delta^\circ G^{tr}$, even in the case of small ions. At present the true criterion controlling the value of the so-called electrostatic term of solvation energy (conception of donor numbers[16], basicity, of the solvent[4]) remains to be revealed, but Born's original model appears to be inappropriate. The objective of this paper was to show one of the possible approaches to evaluation of the determined values of $\Delta^\circ G^{tr}$. The fact that the quantity $\Delta^\circ G^{tr}$ is a very simple function of $\Delta^\circ G^{hydr}$ might facilitate progress in this field of physical chemistry of electrolytes.

REFERENCES

1. Parker A. J., Alexander R.: J. Am. Chem. Soc. *90*, 3313 (1968).
2. Popovych O., Dill A. J.: Anal. Chem. *41*, 456 (1969).
3. Strehlow H. V.: *The Chemistry of Non-Aqueous Solvents.* Vol. I, p. 142. Academic Press, New York and London 1966.
4. Friedman H. L.: J. Phys. Chem. *71*, 1723 (1967).
5. Haugen G. R., Friedman H. L.: J. Phys. Chem. *72*, 4549 (1968).
6. Rais J.: This Journal, in press.
7. Rais J.: *Thesis.* Institute of Nuclear Research, Prague - Řež, 1970.
8. Coetzee J. F., Campion J. J.: J. Am. Chem. Soc. *89*, 2513, 2517 (1967).
9. Krishnan C. V., Friedman H. L.: J. Phys. Chem. *73*, 3934 (1969).
10. Grundwald E., Baughman G., Kohnstam G.: J. Am. Chem. Soc. *82*, 5801 (1960).
11. Alexander R., Ko E. C. F., Parker A. J., Broxton T. J.: J. Am. Chem. Soc. *90*, 5049 (1968).
12. Choux G., Benoit R. L.: J. Am. Chem. Soc. *91*, 6221 (1969).
13. Mischenko K. P., Poltorackij G. M.: *Voprosy Termodinamiki i Strojenija Vodnych i Nevodnych Rastvorov Elektrolytov.* Izd. Chimija, Leningrad 1968.
14. Plambeck J. A.: Can. J. Chem. *47*, 1401 (1969).
15. Arnett E. M., McKelvey D. R.: J. Am. Chem. Soc. *88*, 2598 (1966).
16. Gutmann V.: *Coordination Chemistry in Non-Aqueous Solutions.* Springer, Wien—New York, 1968.
17. Latimer W. M., Pitzer K. S., Slansky C. M.: J. Chem. Phys. *7*, 108 (1939).
18. Pauling L.: *The Nature of the Chemical Bond.* The Oxford University Press, 1940.
19. Criss C. M., Held R. P., Luksha E.: J. Phys. Chem. *72* 2970 (1968).
20. Rais J., Kyrš M., Pivoňková M.: J. Inorg. Nucl. Chem. *30*, 611 (1968).
21. DeLigny C. L., Alfenaar M.: Rec. Trav. Chim. *84*, 81 (1965).
22. Andrews A. L., Benetto H. P., Feakins D., Lawrence K. G., Tomkins R. P. T.: J. Chem. Soc. A, *1968*, 1486.
23. Friedman H. L.: J. Am. Chem. Soc. *76*, 3294 (1954).
24. Miller K. W., Hildebrand J. H.: J. Am. Chem. Soc. *90*, 3001 (1968).
25. Saylor J. H., Battino R.: J. Phys. Chem. *62*, 1334 (1958).
26. Gilles L.: Report CEA-BIB-151 (1969).
27. Krishnan C. V., Friedman H. L.: J. Phys. Chem. *74*, 2356 (1970).

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