410. *Measurements on Thermocells containing Dilute Solutions of Quaternary Ammonium Bromides as Electrolytes.*

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Differences in the thermoelectric powers of thermocells with silver–silver bromide electrodes and dilute aqueous solutions of quaternary ammonium bromides as electrolyte, have been measured for a series of such salts. The results, together with those of some direct Soret coefficient measurements described in the preceding paper, do not support the values for the entropies of transfer of single ions suggested by Goodrich *et al.*[1] on the basis of measurements of thermoelectric power alone.

The initial electrical potential gradient $(\mathrm{d}\phi/\mathrm{d}T)_{\mathrm{sol.}}$ associated with the presence of a thermal gradient in an electrolyte solution of uniform concentration can be expressed (for a uni-univalent salt) as:

$$-\boldsymbol{F}T\,(\mathrm{d}\phi/\mathrm{d}T)_{\mathrm{sol.}} = t_+Q_+^* - t_-Q_-^* \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where t_+ and t_- are the transport numbers, and Q_+^* and Q_-^* the heats of transfer of the positive and the negative ions respectively.[2] These ionic heats of transfer are not experimentally accessible, though they can be obtained in combination. For example, when the

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[1] Goodrich, Goyan, Morse, Preston, and Young, *J. Amer. Chem. Soc.*, 1950, **72**, 4411.

[2] Haase, *Trans. Faraday Soc.*, 1953, **49**, 724.

steady state is reached in such a system, a constant and characteristic concentration gradient coexists with the temperature gradient, and

$$\frac{1}{m}\left(\frac{\mathrm{d}m}{\mathrm{d}T}\right)_{\mathrm{stat.}} = -\frac{Q_+{}^* + Q_-{}^*}{2\boldsymbol{R}T^2}\left(1 + \frac{\partial \ln \gamma_\pm}{\partial m}\right) \equiv -\frac{Q_\pm{}^*}{\boldsymbol{R}T^2}\left(1 + \frac{\partial \ln \gamma_\pm}{\partial m}\right)$$

where m is the molality of the solution. It is possible in principle to measure $m^{-1}(\mathrm{d}m/\mathrm{d}T)_{\mathrm{stat.}}$ and to obtain $(Q_+{}^* + Q_-{}^*)$ as was done, for example, in the preceding paper. The problem of apportioning $(Q_+{}^* + Q_-{}^*)$ between individual ions has attracted some attention.[1, 3, 4] One recently published attempt [1] to do this was based on work carried out under the late Professor Eastman in California, on the initial thermoelectric powers of the cells :

$$\underset{20^\circ}{\mathrm{Ag,AgBr}}|\mathrm{NR_4Br\ in\ water}|\underset{30^\circ}{\mathrm{AgBr,Ag}}$$

$$\underset{20^\circ}{\mathrm{Hg,HgO}}|\mathrm{NR_4OH\ in\ water}|\underset{30^\circ}{\mathrm{HgO,Hg}}$$

R was a *n*-alkyl group, and experiments were carried out with successive members of the series up to the tetra-*n*-pentylammonium compound. The experiments were said to prove that the heats of transfer of large tetra-*n*-alkylammonium ions tended to a constant value, and a kinetic argument was used to justify the conclusion that this constant value was zero. On this basis a table of individual ionic entropies of transfer was compiled. These can be tested by using them to calculate $m^{-1}(\mathrm{d}m/\mathrm{d}T)_{\mathrm{stat.}}$ from eqn. (2). This calculation depends only on the assumption that the heats of entropies of transfer of these large ions tend to a constant value and is independent of the further assumption that they tend to zero. The suggested values of the heats of transfer predict that, for the alkali bromides, the solute should concentrate at the heated end of the solution in 0·01 molal solution.[5] This is not in accord with experience on more concentrated solutions, as can be seen for example from the previous paper and elsewhere.[6] They also predict that the tetra-*n*-alkylammonium bromides should show a negligible Soret effect. The present paper describes some measurements, similar to those made by Goodrich *et al.*,[1] on the initial thermoelectric powers of cells with silver–silver bromide electrodes and solutions of quaternary ammonium bromides as the electrolyte. These are used, in combination with some of the Soret-effect measurements of the previous paper, to examine the validity of the ionic entropies of transfer suggested by Goodrich *et al.*

EXPERIMENTAL

The method used for measuring mean thermoelectric powers between 27° and 32° was based on that described earlier,[7] the cell being modified to permit preliminary saturation of the electrolyte with nitrogen pre-heated to the temperature of the electrolyte and saturated with water vapour by preliminary passage through a solution of potassium bromide of the same concentration as that of the electrolyte in the cell. This procedure has been previously recommended for work with substituted ammonium salts in order to prevent deterioration of the electrode system.[1] The nitrogen stream was interrupted while the e.m.f. measurements were made. Silver–silver bromide electrodes were made as described elsewhere.[8]

Transport numbers of the substituted ammonium cations were obtained by calculating limiting ionic mobilities from conductivity measurements. These were carried out at 25°, with a conventional A.C. Wheatstone bridge with a telephone detector. No correction for changes in the transport number with concentration has been applied, nor for the difference between the mean temperature of the thermocell and the temperature at which these measurements were carried out.

[3] Eastman, *J. Amer. Chem. Soc.*, 1926, **48**, 1482; 1928, **50**, 283, 292.

[4] Wirtz, *Z. Physik*, 1948, **124**, 482.

[5] Tyrrell and Hollis, *J. Amer. Chem. Soc.*, 1951, **73**, 2401.

[6] Tanner, *Trans. Faraday Soc.*, 1927, **23**, 75.

[7] Tyrrell and Hollis, *ibid.*, 1952, **48**, 893.

[8] Chapman and Tyrrell, *ibid.*, 1956, **52**, 1218.

The quaternary ammonium salts, except tetra*iso*pentylammonium bromide, were prepared as described in the preceding paper. Tetra*iso*pentylammonium iodide was prepared by refluxing an excess of *iso*pentyl iodide with tri*iso*pentylamine in dry acetone for 10 hr. After removal of the acetone and cooling, colourless plates of the salt crystallised. Further quantities were obtained by adding acetone and refluxing again. The crystals were purified by dissolution in acetone and reprecipitation with ether. The bromide was prepared in solution by treating a suspension of the iodide with silver oxide and neutralising it with hydrobromic acid to pH 7.

Careful purification of these quaternary salts was essential before use in thermocells. For all salts except the ethylquinolinium bromide, dissolution in absolute alcohol and precipitation with ether, repeated several times, was sufficient. The ethylquinolinium bromide required three crystallisations from absolute alcohol at the temperature of acetone–solid carbon dioxide.

RESULTS AND DISCUSSION

Values[7] of the function P $[\mathrm{d}\phi/\mathrm{d}T - 2{\cdot}303\boldsymbol{R}/z_r\boldsymbol{F}\log m_r + 2{\cdot}303\boldsymbol{R}/z_r\boldsymbol{F}(0{\cdot}8\sqrt{I})]$ calculated from the measured thermoelectric power $\mathrm{d}\phi/\mathrm{d}T$ of the cell: $\text{Ag,AgBr}|\underset{27°}{\text{MBr in}}\ \underset{32°}{\text{H}_2\text{O}}|\text{AgBr,Ag}$ are in Table 1 for 0·01 and 0·10 molal solutions. The cation transport numbers in this Table (apart from those obtained from ref. 1) were calculated by extrapolating measured values of the equivalent conductivities of the quaternary ammonium bromide or iodide to infinite dilution, and assuming the limiting ionic mobility at 25° of the bromide ion to be 78·4 mho l. mole^{-1}, and that of the iodide ion to be 76·85. Tetra*iso*pentylammonium iodide was used in these experiments because the bromide is hygroscopic. These results agree with published values. For example, the cation transference numbers at infinite dilution for tetramethyl-, tetraethyl-, and tetra*iso*pentyl-ammonium cations can be calculated from earlier measurements[9] to be 0·37, 0·30, and 0·17 respectively. The values derived from ref. 1 however differ slightly, probably because they were calculated from a conductivity measurement at a single concentration (0·01 molal).

It has been shown[10] that, for a series of univalent salts with a common anion (say bromide), it is possible to write, ignoring deviations from ideality,

$$\sigma_{\mathrm{NBr}} = -\frac{\boldsymbol{F}}{2\boldsymbol{R}T}\frac{(P_{\mathrm{KBr}} - P_{\mathrm{NBr}})}{t_{\mathrm{N}}} + \frac{t_{\mathrm{K}}}{t_{\mathrm{N}}}\cdot\sigma_{\mathrm{KBr}} = \alpha + \beta\sigma_{\mathrm{KBr}}$$

where σ_{NBr} and σ_{KBr} are the Soret coefficients $(-Q_{\pm}^{*}/\boldsymbol{R}T^2)$ of a salt NBr and of the reference substance KBr; P_{KBr} and P_{NBr} refer to values of the P function calculated from thermoelectric power experiments with KBr and NBr, respectively, as the electrolyte; and t_{K} and t_{N} are the transport numbers of the potassium ion and the cation N^+. The derived quantity P varied slightly with concentration, and values derived from experiments on both 0·01 molal and 0·10 molal solutions, the corresponding values of α- together with the experimental transport numbers at infinite dilution and their ratios β, are shown in Table 1. This Table also includes data from Goodrich *et al.*[1]. The present measurements, obtained at a slightly higher mean temperature, are consistently lower than these where comparison is possible. However the differences, between the results from a given pair of compounds are almost identical.

Soret coefficients can be calculated from these results if a suitable value for the Soret coefficient of potassium bromide is known. From the preceding paper, 2·2 molal potassium bromide has a Soret coefficient of $-1{\cdot}8 \times 10^{-3}$ deg.$^{-1}$. At 0·05 molal and the same mean temperature (30°), Alexander[11] found $-1{\cdot}12 \times 10^{-3}$ deg.$^{-1}$. Unpublished measurements on an 0·01 molal solution with a novel conductometric method[12] have given $-1{\cdot}23 \times 10^{-3}$ deg.$^{-1}$ at 25°, and $-2{\cdot}18 \times 10^{-3}$ at 34·7°. If a value of about $-1{\cdot}5 \times 10^{-3}$

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[9] Bencowitz and Renshaw, *J. Amer. Chem. Soc.*, 1925, **47**, 1904; Kraus and Fuoss, *ibid.*, 1933, **55**, 25; Landolt–Börnstein, Tabellen, Suppl. IIIc, p. 2059.

[10] Tyrrell and Colledge, *Trans. Faraday Soc.*, 1954, **50**, 1056.

[11] Alexander, *Z. phys. Chem. (Leipzig)*, 1954, **203**, 213.

[12] Personal communication from Dr. J. N. Agar.

deg.$^{-1}$ is chosen for potassium bromide in 0·01 and 0·1 molal solution at a mean temperature of 30°, approximate coefficients may be calculated for the quaternary ammonium salts (Table 2). These are compared with directly measured values, uncorrected for deviations from ideality, obtained from the preceding paper.

TABLE 1. *Values of the function P, and of the constants α and β for quaternary ammonium bromides.*

Cation	Transport number of cation at inf. diln.	β	0·01 Molal		0·10 Molal	
			P (μv/deg.$^{-1}$)	α (10^3 deg.$^{-1}$)	P (μv/deg.$^{-1}$)	α (10^3 deg.$^{-1}$)
K …………………	0·48	—	+358	—	+347	—
NMe_4 ……………	0·36	1·3	+287	− 3·7	+274	−3·9
NEt_4 ……………	0·29	1·7	+237	− 7·9	+229	−7·7
$N(CH_2Bu^i)_4$ ……	0·20	2·4	+310	− 4·6	(+198 at 0·047M.)	—
$NPhMe_3$ ………	0·31	1·5	+310 †	− 2·9	+253 †	−5·7
1-Ethylpyridinium ………	0·34	1·4	+314	− 2·4	+264	−4·6
1-Ethylquinolinium ………	0·25	1·9	+303	− 4·2	+245	−7·8
K * ……………	0·48	—	+382	—	—	—
NMe_4 * …………	0·34	1·4	+310	− 4·1	—	—
NEt * …………	0·26	1·8	+283	− 7·4	—	—
NPr^n_4 * …………	0·19	2·5	+279	−10·5	—	—
NBu^n_4 * ………	0·16	3·0	+280	−12·3	—	—
$N(CH_2Bu^n)_4$ * …	0·14	3·4	+281	−13·7	—	—

* From ref. 1; thermoelectric measurements between 20° and 30°.

† These results are less certain than the rest because of experimental difficulties.

TABLE 2. *Approximate Soret coefficients, $m^{-1}(\mathrm{d}m/\mathrm{d}T_{\mathrm{stat.}})$ of quaternary ammonium salts in aqueous solution.*

Salt	T_m	Calc. from data in Table 1		Directly by Tanner's method (10^{-3} deg.$^{-1}$) at T_m 30° (molalility in parentheses)
		0·01 molal (10^{-3} deg.$^{-1}$)	0·10 molal (10^{-3} deg.$^{-1}$)	
NMe_4Br ……………………………	29·5°	− 6	− 6	−6·5 (2·5m)
	25	− 6	—	−4·6 (1·13m)
NEt_4Br ……………………………	29·5	−10	−10	—
	25	−10	—	−8·7 (1·80m)
$N(CH_2Bu^i)_4Br$ …………………	29·5	− 8	—	?0 for iodide and chloride
$NPhMe_3Br$ ………………………	29·5	− 5	− 8	−7·0 (0·53m)
1-Ethylpyridinium bromide …	29·5	− 5	− 7	∼−5·5 (2·01m)
1-Ethylquinolinium bromide …	29·5	− 7	−11	∼−12 for iodide (0·52m)
$N(CH_2Bu^n)_4Br$ …………………	25	−19	—	—

In view of the high and varied concentrations at which the direct measurements were done, and the fact that the values have not been corrected for deviations from ideality, the agreement is astonishingly good. It certainly proves that there is no evidence for the belief that any of the quaternary ammonium salts in aqueous solution examined have Soret coefficients close to zero. The sole exceptions to this were solutions of tetra*iso*pentylammonium chloride and iodide. These salts are not very soluble in water and are not therefore suited to examination by the Tanner method. In neither case did the experiments proceed normally, and the apparently zero value for the Soret coefficient is very doubtful, especially in view of the thermoelectric evidence. A further confirmation of the large negative Soret coefficient of tetraethylammonium bromide has recently been obtained: a conductometric determination [12] in 0·01 molal solution at a mean temperature of 25° gave $-6·15 \times 10^{-3}$ deg.$^{-1}$.

There seems no reasonable doubt that the table of ionic entropies of transfer suggested by Goodrich *et al.*[1] is unsatisfactory, at least as far as the bromide series is concerned. This can be attributed to the very scanty experimental evidence for the conclusion that the heats (or entropies) of transfer of large symmetrical tetra-alkylammonium ions tend to a constant value. They wrote, using the sign convention that the heated electrode is positive,

$$-\boldsymbol{F}\,.\,\mathrm{d}\phi/\mathrm{d}T = (S_{+}^{*} + S_{-}^{*})t_{+} + (\Delta S_{\mathrm{R}} - S_{-}^{*})$$

where ΔS_{R} was the entropy change in the electrode reaction. Their experimental results are displayed in Fig. 4 of their paper, and it is claimed that the points for tetra-*n*-propyl, -butyl, and -pentyl salts lie on a straight line. These could, with as much justification, be said to be near the crest of a curve. The claim is rather more convincing for the hydroxide series, and, in fact, Soret coefficients calculated for hydroxides from these data are reasonably satisfactory in a semiquantitative way. This simply means that the table of ionic entropies for the hydroxide series in ref. (1) is probably roughly correct as a *conventional* scale with an arbitrary choice of $S_{+}^{*} = 0$ for a large tetra-alkylammonium ion. The agreement found between the ionic entropies of transfer of cations calculated from the independent experiments on bromides and hydroxides can hardly be more than fortuitous.

It is our opinion that no significance should be attached to any of the tables of heats or entropies of transfer of individual ions which have hitherto been published. There seems to be no reason why a satisfactory table, with a conventional zero, should not be constructed when sufficient accurate experimental results on Soret coefficients, especially in dilute solution, are available. Such a table must of course be consistent with the experimental measurements on thermocells.

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