# Studies in Some ' Isodielectric ' Media. Part III.[1] Standard Potentials of M/M$^+$ (M = Li, Na, and K) Electrodes in Methanol–Propylene Glycol

By **K. K. Kundu,* A. K. Rakshit, and M. N. Das,*** Physical Chemistry Laboratories, Jadavpur University, Calcutta-32, India

Standard potentials ($_sE°$) of M/M$^+$ (M = Li, Na, or K) electrodes have been determined at 25° in the ' isodielectric ' methanol–propylene glycol solvent system from the measured e.m.f. values of the cell $M_y$(Hg)/MBr($m$), solvent/-AgBr–Ag. These potentials as well as the known ($_sE°$) values of the AgX–Ag (X = Cl or Br) electrode furnished the standard potentials ($_sE_{cell}°$) of the complete cells comprising the M/M$^+$ and AgX–Ag electrodes. The standard free-energy changes $\Delta G_t°$(MX) accompanying the transfer of MX from methanol to the other solvents have been computed and are found to depend chiefly on the ion–dipole interactions, as the ' electrostatic effect ' is relatively small in this solvent system. The values of $\Delta G_t°$(i) for the individual ions, computed from the ' simultaneous extrapolation ' of the observed linear plots of $\Delta G_t°$(MCl) and $\Delta G_t°$(KCl–MCl) against $(r_{M^+})^{-1}$ (M = Li, Na, or K), to $(r_{M^+})^{-1} = 0$, suggest that the cations are methanophilic and that the anions are glycophilic. The variation of $\Delta G_t°$(i) values with the solvent composition is found to be in fairly good agreement with what is expected from the consideration of the interaction energies of these ionic species with positive or negative charge centres of the isolated solvent dipoles. Also the values of $\Delta G_t°(H^+)$ for H$^+$ seem to indicate that methanol is more ' basic ' than propylene glycol.

PART I of this series[2] reported $_sE°$ values of AgX–Ag (X = Cl or Br) electrodes in a series of approximately isodielectric solvents formed by mixing methanol and propylene glycol (PG). Here we report studies on the $_sE°$ values of M/M$^+$ electrodes (M = Li, Na, or K) at 25° in the same solvent system. This study was undertaken since the $_sE°$ values of Ag–AgX electrodes in these media should be useful in understanding the relative behaviour of MX type electrolytes in ' isodielectric ' media in which the ' electrostatic effect '[3,4] is negligibly small.

The method used was similar to that described earlier[4] in the case of glycol–water. Cell A was used in conjunction with Cell B, the concentration of the metal in the amalgam being the same in A and B (M = Li, Na, or K).

$$M_y(Hg)|MBr(m), \text{ solvent}|AgBr\text{–}Ag \qquad A$$

$$M_y(Hg)|MBr\ (0{\cdot}1,\ 0{\cdot}2, \text{ and } 0{\cdot}5m), \text{ water}|AgBr\text{–}Ag \qquad B$$

The cell B furnished the e.m.f. correction ($E_{corr}$) that arises from the activity of the metal in amalgam $M_y$(Hg) used in the cell A. This is related to the observed e.m.f. values ($E_B$) of the cell B, the standard potentials ($_wE°$) of M/M$^+$ and AgBr–Ag electrodes, and the mean activity coefficients ($\gamma_\pm$) of MBr solution in water at the respective concentrations by equation (1), where $k = 2{\cdot}303\ RT/F$, the subscript w denotes that the values are referred to water, and $m$ is molal concentration.

$$\begin{aligned} E_{corr} &= -k \log a_{M_y}(Hg) \\ &= {}_wE_{M/M^+}° + {}_wE_{AgBr\text{-}Ag}° - E_B - 2k \log m\gamma_\pm \qquad (1) \end{aligned}$$

The values of the standard potential of the cell A, $(_sE_{cell}°)_A$ obtained after Hitchcock's extrapolation procedure,[5] along with the respective values of $E_{corr}$ furnished the standard potential ($_sE_{cell}°$) of the cell C,

$$M|MX, \text{ solvent}|AgX\text{–}Ag \qquad C$$

where X = Br, in each of the solvents.

## EXPERIMENTAL

The general experimental details were essentially similar to those described earlier.[2,4] After the insertion of the electrodes in the respective compartments of the cell containing the electrolyte solution, an initial period of *ca.* 45 min was allowed for the attainment of equilibrium. 2—3 Readings at 10 min-intervals were taken for a further period of 20—30 min to ensure that a stable potential had been reached. For each system, 2 or 3 concentrations were used for checking. Concentrations below 0·010m or so were avoided in view of the uncertainties caused by the action of the amalgam on these solvents and decreased sensitivity of the readings due to the higher resistance of the solutions in glycol-rich solvents.

## RESULTS

The observed e.m.f. values ($E_A$) of the cell A and the corresponding molalities of MBr for each of the solvents are in Tables 1—3. The values were taken as positive when the reference electrodes were connected to the positive terminal of the potentiometer.

The standard potentials $(_sE_{cell}°)_A$ of cell A were obtained from the plots of the Hitchcock-type[4] function $E'$, defined by equation (2), against $m$ by extrapolation to $m = 0$.

$$\begin{aligned} E' &= E_A + 2k \log m_{MBr} - 2kS_f m^{\frac{1}{2}} d_s^{\frac{1}{2}} - 2k \log (1 + 0{\cdot}002mM_s) \\ &= (_sE°)_{M/M^+} + (_sE°)_{AgBr\text{-}Ag} + k \log a_{M_y(Hg)} + f(m) \\ &= (_sE_{cell}°)_A + f(m) \qquad (2) \end{aligned}$$

The dielectric constants ($D_s$) and the densities ($d_s$) of the solvents and $S_f$ values are reported in Part I.[2] The values of $E'$ plotted against $m$ resulted in fairly good straight lines, and the values of $(_sE_{cell}°)_A$ obtained by extrapolation are presented at the bottom of Tables 1—3. The average standard deviation amounts to about ±0·7 mV.

The observed e.m.f. values ($E_B$) of the cells of the type B, for 0·1, 0·2, and 0·5m of the respective metal bromides in each case, along with the mean value of $E_{corr}$ computed

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[1] Part II, K. K. Kundu, A. L. De, and M. N. Das, preceding paper.

[2] Part I, K. K. Kundu, A. L. De, and M. N. Das, *J.C.S. Dalton*, 1972, 373.

[3] R. G. Bates, in ' Hydrogen-Bonded Solvent Systems,' eds. A. K. Covington and P. Jones, Taylor and Francis, London, 1968, pp. 49—81.

[4] K. K. Kundu, A. K. Rakshit, and M. N. Das, *Electrochim. Acta*, submitted for publication.

[5] D. I. J. Hitchcock, *J. Amer. Chem. Soc.*, 1928, **50**, 2076.

TABLE 1

E.m.f. ($E$) of cells A and B in methanol–propylene glycol at 25° (M = Li)

| Methanol | | 30% PG | | 50% PG | | 70% PG | | 90% PG | | 100% PG | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| $m$ [a] | $E$/V | $m$ | $E$/V | $m$ | $E$/V | $m$ | $E$/V | $m$ | $E$/V | $m$ | $E$/V |
| | | | | | Cell A | | | | | | |
| 0·0284 | 2·2030 | 0·0335 | 2·1855 | 0·0250 | 2·1926 | 0·0156 | 2·1888 | 0·0153 | 2·1722 | 0·0294 | 2·1706 |
| 0·0484 | 2·1810 | 0·0525 | 2·1670 | 0·0313 | 2·1837 | 0·0347 | 2·1587 | 0·0311 | 2·1458 | 0·0296 | 2·1722 |
| 0·0641 | 2·1730 | 0·0615 | 2·1638 | 0·0433 | 2·1721 | 0·0427 | 2·1510 | 0·0497 | 2·1300 | 0·0426 | 2·1588 |
| 0·0806 | 2·1614 | 0·0657 | 2·1611 | 0·0521 | 2·1657 | 0·0664 | 2·1363 | 0·0660 | 2·1204 | 0·0547 | 2·1522 |
| 0·1007 | 2·1554 | 0·0736 | 2·1561 | 0·0663 | 2·1572 | 0·0739 | 2·1323 | 0·0820 | 2·1152 | 0·0641 | 2·1485 |
| 0·1168 | 2·1498 | 0·0898 | 2·1499 | 0·0839 | 2·1484 | 0·0902 | 2·1259 | 0·1009 | 2·1068 | 0·0844 | 2·1409 |
| | | 0·0988 | 2·1466 | 0·0998 | 2·1431 | | | | | | |
| $({}_sE_{\mathrm{cell}}^\circ)_A$ = | 1·9908 | $({}_sE_{\mathrm{cell}}^\circ)_A$ = | 1·9780 | $({}_sE_{\mathrm{cell}}^\circ)_A$ = | 1·9720 | $({}_sE_{\mathrm{cell}}^\circ)_A$ = | 1·9490 | $({}_sE_{\mathrm{cell}}^\circ)_A$ = | 1·9304 | $({}_sE_{\mathrm{cell}}^\circ)_A$ = | 1·9496 |
| | | | | | Cell B | | | | | | |
| 0·10 | 2·2756 | 0·10 | 2·2750 | 0·10 | 2·2780 | 0·10 | 2·2556 | 0·10 | 2·2583 | 0·10 | 2·2826 |
| 0·20 | 2·2432 | 0·20 | 2·2420 | 0·20 | 2·2452 | 0·20 | 2·2323 | 0·20 | 2·2244 | 0·20 | 2·2494 |
| 0·50 | 2·1970 | 0·50 | 2·1953 | 0·50 | 2·1983 | 0·50 | 2·1873 | 0·50 | 2·1784 | 0·50 | 2·2034 |
| $E_{\mathrm{corr(mean)}}$ = | 0·969 | $E_{\mathrm{corr(mean)}}$ = | 0·971 | $E_{\mathrm{corr(mean)}}$ = | 0·968 | $E_{\mathrm{corr(mean)}}$ = | 0·980 | $E_{\mathrm{corr(mean)}}$ = | 0·988 | $E_{\mathrm{corr(mean)}}$ = | 0·963 |

[a] $m$ Is molal concentration throughout.

TABLE 2

E.m.f. ($E$) of the cells A and B in methanol–propylene glycol at 25° (M = Na)

| Methanol | | 30% PG | | 50% PG | | 70% PG | | 100% PG | |
|---|---|---|---|---|---|---|---|---|---|
| $m$ | $E$/V | $m$ | $E$/V | $m$ | $E$/V | $m$ | $E$/V | $m$ | $E$/V |
| | | | | Cell A | | | | | |
| 0·0150 | 1·9154 | 0·0151 | 2·0182 | 0·0132 | 1·9554 | 0·0132 | 2·0373 | 0·0142 | 2·0084 |
| 0·0202 | 1·9042 | 0·0282 | 1·9923 | 0·0321 | 1·9240 | 0·0164 | 2·0275 | 0·0171 | 2·0016 |
| 0·0331 | 1·8818 | 0·0432 | 1·9756 | 0·0452 | 1·9097 | 0·0322 | 2·0096 | 0·0393 | 1·9731 |
| 0·0462 | 1·8698 | 0·0553 | 1·9674 | 0·0541 | 1·9031 | 0·0488 | 1·9892 | 0·0602 | 1·9594 |
| 0·0680 | 1·8530 | 0·0643 | 1·9609 | 0·0703 | 1·8938 | 0·0539 | 1·9833 | 0·0641 | 1·9585 |
| 0·0732 | 1·8496 | 0·0682 | 1·9575 | 0·0888 | 1·8849 | 0·0699 | 1·9758 | 0·0799 | 1·9532 |
| 0·0908 | 1·8395 | 0·0934 | 1·9455 | — | — | 0·0809 | 1·9704 | 0·0928 | 1·9491 |
| 0·1022 | 1·8357 | 0·0992 | 1·9437 | — | — | 0·0929 | 1·9662 | | |
| $({}_sE_{\mathrm{cell}}^\circ)_A$ = | 1·6784 | $({}_sE_{\mathrm{cell}}^\circ)_A$ = | 1·7804 | $({}_sE_{\mathrm{cell}}^\circ)_A$ = | 1·7116 | $({}_sE_{\mathrm{cell}}^\circ)_A$ = | 1·7900 | $({}_sE_{\mathrm{cell}}^\circ)_A$ = | 1·7620 |
| | | | | Cell B | | | | | |
| 0·10 | 1·9988 | 0·10 | 2·0999 | 0·10 | 2·0322 | 0·10 | 2·1096 | 0·10 | 2·0799 |
| 0·20 | 1·9658 | 0·20 | 2·0684 | 0·20 | 2·0000 | 0·20 | 2·0775 | 0·20 | 2·0482 |
| 0·50 | 1·9226 | 0·50 | 2·0250 | 0·50 | 1·9547 | 0·50 | 2·0337 | 0·50 | 2·0050 |
| $E_{\mathrm{corr(mean)}}$ = | 0·917 | $E_{\mathrm{corr(mean)}}$ = | 0·815 | $E_{\mathrm{corr(mean)}}$ = | 0·884 | $E_{\mathrm{corr(mean)}}$ = | 0·806 | $E_{\mathrm{corr(mean)}}$ = | 0·835 |

TABLE 3

E.m.f. ($E$) of the cells A and B in methanol–propylene glycol at 25° (M = K)

| Methanol | | 30% PG | | 50% PG | | 70% PG | | 90% PG | | 100% PG | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| $m$ | $E$/V | $m$ | $E$/V | $m$ | $E$/V | $m$ | $E$/V | $m$ | $E$/V | $m$ | $E$/V |
| | | | | | Cell A | | | | | | |
| 0·0182 | 2·0036 | 0·0129 | 2·0239 | 0·0206 | 1·9912 | 0·0193 | 2·0281 | 0·0246 | 2·0396 | 0·0171 | 2·0443 |
| 0·0208 | 1·9985 | 0·0299 | 1·9892 | 0·0251 | 1·9843 | 0·0323 | 2·0081 | 0·0406 | 2·0238 | 0·0280 | 2·0243 |
| 0·0331 | 1·9784 | 0·0367 | 1·9815 | 0·0323 | 1·9751 | 0·0477 | 1·9953 | 0·0521 | 2·0155 | 0·0448 | 2·0066 |
| 0·0456 | 1·9656 | 0·0426 | 1·9736 | 0·0428 | 1·9613 | 0·0736 | 1·9830 | 0·0666 | 2·0082 | 0·0613 | 1·9953 |
| 0·0603 | 1·9552 | 0·0664 | 1·9584 | 0·0561 | 1·9547 | 0·0821 | 1·9781 | 0·0822 | 2·0019 | 0·0668 | 1·9915 |
| 0·0857 | 1·9401 | 0·0866 | 1·9464 | 0·0813 | 1·9434 | 0·1049 | 1·9715 | 0·0989 | 1·9973 | 0·0748 | 1·9877 |
| | | | | | | | | | | 0·0943 | 1·9788 |
| $({}_sE_{\mathrm{cell}}^\circ)_A$ = | 1·7740 | $({}_sE_{\mathrm{cell}}^\circ)_A$ = | 1·7784 | $({}_sE_{\mathrm{cell}}^\circ)_A$ = | 1·7626 | $({}_sE_{\mathrm{cell}}^\circ)_A$ = | 1·7940 | $({}_sE_{\mathrm{cell}}^\circ)_A$ = | 1·8164 | $({}_sE_{\mathrm{cell}}^\circ)_A$ = | 1·8080 |
| | | | | | Cell B | | | | | | |
| 0·10 | 2·1017 | 0·10 | 2·0964 | 0·10 | 2·0723 | 0·10 | 2·0975 | 0·10 | 2·1192 | 0·10 | 2·1027 |
| 0·20 | 2·0701 | 0·20 | 2·0634 | 0·20 | 2·0410 | 0·20 | 2·0660 | 0·20 | 2·0863 | 0·20 | 2·0710 |
| 0·50 | 2·0272 | 0·50 | 2·0216 | 0·50 | 1·9990 | 0·50 | 2·0235 | 0·50 | 2·0443 | 0·50 | 2·0285 |
| $E_{\mathrm{corr(mean)}}$ = | 1·026 | $E_{\mathrm{corr(mean)}}$ = | 1·032 | $E_{\mathrm{corr(mean)}}$ = | 1·055 | $E_{\mathrm{corr(mean)}}$ = | 1·030 | $E_{\mathrm{corr(mean)}}$ = | 1·009 | $E_{\mathrm{corr(mean)}}$ = | 1·025 |

from equation (1), are also given in the respective Tables. The relevant data for computing the $E_{corr}$ values were obtained from the literature.[6,7] In each case the $E_{corr}$ values for the three concentrations lie within ±1 mV of the reported mean value.

The standard potentials $({}_{s}E_{cell}°)$ of the cells C, presented in Table 4, were computed by using equation (3).

$$({}_{s}E_{cell}°)_{C} = {}_{s}E_{M/M^{+}}° + {}_{s}E_{AgBr\text{–}Ag}° = ({}_{s}E_{cell}°)_{A} - k \log a_{M_{y}(Hg)} = ({}_{s}E_{cell}°)_{A} + E_{corr} \quad (3)$$

The standard potentials ${}_{s}E_{M/M^{+}}°$ in each solvent were computed from these values of $({}_{s}E_{cell}°)_{C}$ by subtracting the ${}_{s}E°$ values of the AgBr–Ag electrode in the respective solvents reported in Part I.[2] Since the mean error in the values of $E_{corr}$ is of the order of ±1 mV, the maximum probable error in the values of ${}_{s}E°$ of the M/M$^{+}$ electrodes in these solvents should be of the order of ±2 mV. The values of $({}_{s}E_{cell}°)_{C}$ of the cell C comprising the AgCl–Ag electrode were also computed by coupling the ${}_{s}E_{M/M^{+}}°$ values with ${}_{s}E°$ values of the Ag–AgCl electrode in the respective solvents.[2]

TABLE 4

Standard potentials $[({}_{s}E_{cell}°)_{C}{}^{m}/V]$ of the cell C in methanol–propylene glycol at 25°

| Wt. % PG | M = H [a] |  | M = Li |  | M = Na |  | M = K |  |
|---|---|---|---|---|---|---|---|---|
|  | X = Cl | X = Br | X = Cl | X = Br | X = Cl | X = Br | X = Cl | X = Br |
| 0 | −0·0090 | −0·1340 | 3·085 | 2·960 | 2·720 | 2·595 | 2·925 | 2·800 |
| 30 | −0·0070 | −0·1320 | 3·074 | 2·949 | 2·720 | 2·595 | 2·935 | 2·810 |
| 50 | −0·0100 | −0·1355 | 3·066 | 2·940 | 2·722 | 2·596 | 2·943 | 2·818 |
| 70 | −0·0170 | −0·1445 | 3·057 | 2·929 | 2·724 | 2·596 | 2·952 | 2·824 |
| 90 | −0·0275 | −0·1550 | 3·046 | 2·918 | (2·725) [b] | (2·597) [b] | 2·953 | 2·825 |
| 100 | −0·0320 | −0·1633 | 3·044 | 2·913 | 2·728 | 2·597 | 2·964 | 2·833 |

[a] Ref 2. [b] Values in parentheses were obtained from interpolation.

The standard potentials of the cell C (M = H, Li, Na, or K; X = Cl or Br) in each of the solvents are presented in Table 4. These values are referred to the molal scale and denoted by $({}_{s}E_{cell}°)_{C}{}^{m}$. The values of ${}_{s}E_{M/M^{+}}°$ presented in Table 5, are, of course, independent of the scale effect.

TABLE 5

Standard potentials $({}_{s}E°)$ of the M/M$^{+}$ electrodes in methanol–propylene glycol at 25°

| Wt. % PG | ${}_{s}E_{Li/Li^{+}}°/V$ | ${}_{s}E_{Na/Na^{+}}°/V$ | ${}_{s}E_{K/K^{+}}°/V$ |
|---|---|---|---|
| 0 | 3·094 | 2·729 | 2·934 |
| 30 | 3·081 | 2·727 | 2·942 |
| 50 | 3·076 | 2·732 | 2·953 |
| 70 | 3·074 | 2·741 | 2·969 |
| 90 | 3·073 | 2·752 | 2·980 |
| 100 | 3·076 | 2·760 | 2·996 |

The ${}_{s}E°$ values of Li/Li$^{+}$ and Na/Na$^{+}$ electrodes in methanol from this study are within ±2 mV of the literature data,[8] but the corresponding value for the K/K$^{+}$ electrode deviates by 13 mV from the value of 2·921 V determined by Strehlow and his co-workers.[9]

## DISCUSSION

The standard free-energy changes $\Delta G_{t}°(MX)$ accompanying the transfer process, have been computed

$$\text{MX (methanol, MH)} \longrightarrow \text{MX (solvent, SH)}$$

by equation (4), where $(E_{cell}°)_{C}{}^{N}$ is the standard

$$\Delta G_{t}°(MX) = -F[({}_{s}E_{cell}°)_{C}{}^{N} - ({}_{m}E_{cell}°)_{C}{}^{N}] \quad (4)$$

potential of the cell C on the mole fraction scale and the subscripts m and s refer to the corresponding quantities in methanol and the solvent respectively. The values of $(E_{cell}°)_{C}{}^{N}$ were obtained from the reported values of $(E_{cell}°)_{C}{}^{N}$ by the usual relation. The values of $\Delta G_{t}°(MX)$ for different electrolytes in these solvents are recorded in Table 6. The variations of $\Delta G_{t}°(MX)$ for the different metal bromides against wt. % PG have been compared in Figure 1. $\Delta G_{t}°(MX)$ for NaCl has been included in the Figure to illustrate the relative behaviour of the two halide ions (Cl$^{-}$ and Br$^{-}$).

Figure 1 and Table 6 show that for KBr and NaBr $\Delta G_{t}°(MX)$ becomes increasingly negative as the proportion of PG increases, the values for KBr being more negative than for NaBr. The corresponding values for LiBr are slightly positive. The behaviour of HBr is, however, different from that of alkali-metal

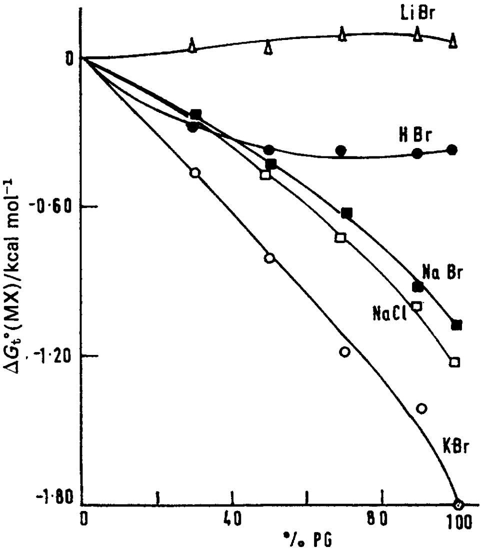

FIGURE 1 Variation of $\Delta G_{t}°(MX)$ with wt. % propylene glycol

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[6] R. A. Robinson and R. H. Stokes, ' Electrolyte Solutions,' 2nd rev. edn., Butterworths, London, 1965.

[7] W. M. Latimer, ' Oxidation Potentials,' 2nd edn., Prentice Hall, Englewood Cliff, 1952.

[8] A. Macfarlane and H. Hartley, *Phil. Mag.*, 1929, **8**, 320; H. Hartley and A. Macfarlane, *ibid.*, 1935, **10**, 611.

[9] K. Brauer and H. Strehlow, *Z. physik. Chem.* (*Frankfurt*), 1958, **17**, 346.

bromides, as indicated by a flat minimum (Figure 1). The distinctive behaviour must be due to the peculiar nature of $H^+$ which is not only unique in its size but has also the ability of undergoing ' chemical ' solvation, with the amphiprotic solvent molecules acting as base. The overall effect of gradual addition of PG to methanol is that the transfer of alkali-metal bromides becomes increasingly spontaneous in the case of KBr, less so in the case of NaBr, and slightly non-spontaneous in the case of LiBr. Thus, the ' escaping ' tendency of the metal bromides, and for that matter other halides as well, decreases in the order: KBr > NaBr > LiBr. Since $Br^-$ is common to these salts, this order necessarily represents the order for the alkali-metal cations.

TABLE 6

Standard free energy of transfer [$\Delta G_t°(MX)$/kcal mol$^{-1}$] of some electrolytes (MX) from methanol to methanol–propylene glycol at 25°

| Wt. % PG | M = H[a] |  | M = Li |  | M = Me |  | M = K |  |
|---|---|---|---|---|---|---|---|---|
|  | X = Cl | X = Br | X = Cl | X = Br | X = Cl | X = Br | X = Cl | X = Br |
| 30 | −0·27 | −0·27 | 0·04 | 0·04 | −0·23 | −0·23 | −0·46 | −0·46 |
| 50 | −0·39 | −0·37 | 0·02 | 0·04 | −0·46 | −0·44 | −0·85 | −0·83 |
| 70 | −0·44 | −0·37 | 0·02 | 0·09 | −0·72 | −0·65 | −1·25 | −1·18 |
| 90 | −0·46 | −0·39 | 0·02 | 0·09 | −0·99 | −0·92 | −1·52 | −1·45 |
| 100 | −0·51 | −0·37 | −0·09 | 0·05 | −1·22 | −1·08 | −1·94 | −1·80 |

[a] Interpolated values.

Again, from Table 6 and Figure 1, the relative values of $\Delta G_t°(MX)$ for X = Cl and Br at any composition are in the order: NaCl > NaBr; and $Na^+$ being common, the ' escaping ' tendency of $Cl^-$ and $Br^-$ ions thus increases as the size of the anion decreases.

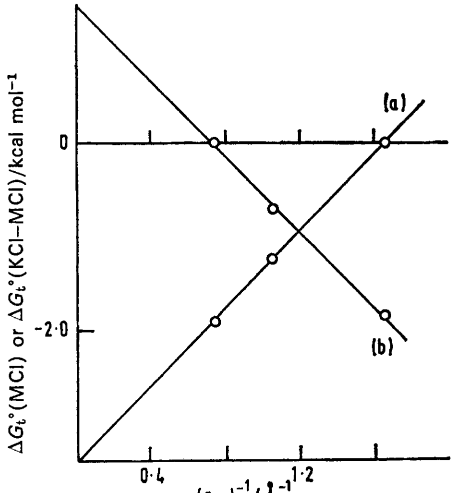

FIGURE 2 Typical ' simultaneous extrapolation ' of (a) $\Delta G_t°(MCl)$ and (b) $\Delta G_t°(KCl–MCl)$ *vs.* $(r_{M^+})^{-1}$ in propylene glycol

An attempt may be made to evaluate the standard free energies of transfer $\Delta G_t°(i)$ for individual ions. A method of extrapolation based essentially on those of Izmailov and his co-workers [10,11] and Feakins and his co-workers [12,13] has been used for computing $\Delta G_t°(i)$ values. The values of $\Delta G_t°(MCl)$ and $\Delta G_t°(KCl - MCl)$ *i.e.* $\Delta G_t°(K^+ - M^+)$ were simultaneously plotted against $(r_{M^+})^{-1}$, which on extrapolation to $(r_{M^+})^{-1} = 0$ gave $[\Delta G_t°(Cl^-) - 2{\cdot}303\,RT \log M_s/M_m]$ and $[\Delta G_t°(K^+) + 2{\cdot}303\,RT \log M_s/M_m]$ respectively. In each case the plots were found to result in fairly good straight lines, as illustrated in Figure 2 for 100% PG. The ' simultaneous extrapolation ' was intended to provide the least discrepancy between the sum of the extrapolated values of $\Delta G_t°(Cl^-)$ and $\Delta G_t°(K^+)$ and the experimental values of $\Delta G_t°(KCl)$, in order to give greater confidence in the extrapolated values. The extrapolated values have uncertainties of the order of ±0·1 kcal/g-ion. The values of $\Delta G_t°(Cl^-)$ and $\Delta G_t°(K^+)$ for each solvent were of use in computing $\Delta G_t°(i)$ values for the other ions. The values so obtained are reported in Table 7.

TABLE 7

Standard free energy of transfer [$\Delta G_t°(i)$/kcal g-ion$^{-1}$] of some individual ions from methanol to methanol–propylene glycol (PG) at 25°

| Wt. % PG | $H^+$ | $Li^+$ | $Na^+$ | $K^+$ | $Cl^-$ | $Br^-$ |
|---|---|---|---|---|---|---|
| 30 | 0·46 | 0·77 | 0·50 | 0·27 | −0·73 | −0·73 |
| 50 | 0·91 | 1·32 | 0·84 | 0·45 | −1·30 | −1·28 |
| 70 | 1·52 | 1·98 | 1·24 | 0·71 | −1·96 | −1·89 |
| 90 | 2·01 | 2·39 | 1·48 | 0·95 | −2·47 | −2·40 |
| 100 | 2·42 | 2·84 | 1·71 | 0·99 | −2·93 | −2·79 |

The transfer free energies of cations, $\Delta G_t°(M^+)$, from methanol to the solvents containing increasing proportion of PG, become increasingly positive, indicating that the cations are methanophilic. The relative magnitudes of the values of $\Delta G_t°(M^+)$ for different alkali-metal cations in any solvent are in the order: $K^+ < Na^+ < Li^+$, which is the order of decreasing ion size. On the other hand, the values of $\Delta G_t°(Cl^-)$ as well as $\Delta G_t°(Br^-)$ become more negative with increasing proportion of PG in the solvent mixture, the magnitude of $\Delta G_t°(Br^-)$ being larger than that of $\Delta G_t°(Cl^-)$ at any solvent composition (Table 7), which suggests that the anions are glycophilic.

The ' electrostatic contribution ' $\Delta G_{t,el}°(i)$ in these

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[10] V. V. Aleksandrov and N. A. Izmailov, *Zhur. fiz. Khim.*, 1958, **32**, 404.

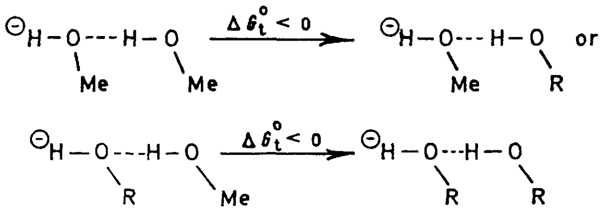
[11] N. A. Izmailov, *Doklady Akad. Nauk*, 1959, **127**, 104; *Zhur. fiz. Khim.*, 1960, **34**, 2414.

[12] D. Feakins and P. Watson, *Chem. and Ind.*, 1960, 2008; *J. Chem. Soc.*, 1963, 4686, 4734.

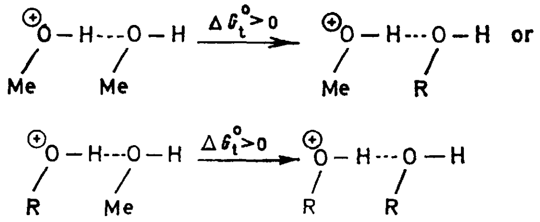
[13] A. L. Andrews, H. P. Bennetto, D. Feakins, K. G. Lawrence, and R. P. T. Tomkins, *J. Chem. Soc.* (*A*), 1968, 1486.

'isodielectric' media being negligibly small, the observed $\Delta G_t^\circ(i)$ values should largely reflect the 'chemical' contribution, $\Delta G_{t,ch}^\circ(i)$, arising from solvation. It is expected that the relative affinities exerted by methanolic dipoles in the case of cations and that by glycolic dipoles in the case of anions should arise from the relative solvating capacities of methanolic or glycolic dipoles. Due to the inductive effect of the methyl group in methanol, the negative charge density on the oxygen atom, ${}^{m}\Delta^-$ should be somewhat larger than the corresponding quantity ${}^{g}\Delta^-$ in PG, where the presence of two $-OH$ groups in suitable proximity is likely to favour intramolecular hydrogen bond formation as in ethylene glycol.[4] As a result, the protonic character of the hydrogen atom of the $-OH$ group in methanol, ${}^{m}\delta^+$ is less than that in PG, ${}^{g}\delta^+$. That is, one may imagine at least qualitatively that ${}^{m}\Delta^- > {}^{g}\Delta^-$ and ${}^{m}\delta^+ < {}^{g}\delta^+$.

Hence, it is expected that for an anion



and for a cation



Furthermore, the observed magnitudes of the $\Delta G_t^\circ(i)$ values for anions or cations also conform with what is expected from the relative surface charge density of the ions.

It may be pointed out here that though the effect of secondary solvation[14] arising from the difference in the permittivity of the solvents is negligibly small in these 'isodielectric' media, another part of it, arising especially in the vicinity of the primary solvated ions where the solvent molecules can be looked upon as a 'structureless dipole',[15] may be somewhat significant because of the difference in dipole moments of the two types of solvent molecules. This contribution, however, is likely to be less significant than that involved in the primary solvation zone. As a result, the tentative molecular picture of the transfer process given above should remain largely unaltered.

The positive values of $\Delta G_t^\circ(H^+)$, which increase with PG content, support the conclusions reached earlier (Part I) that methanol is more basic than PG. Since the main effect of the secondary solvation, *i.e.* $\Delta G_{t,el}^\circ(H^+)$, is relatively small in these 'isodielectric media' and if the radii of the solvated $H^+$ in the two solvents are similar, the conclusion regarding the relative basicity of these solvents may be approximately correct, though Franks and Ives[16] and Popovych[17] recently expressed doubts about such conclusions regarding solvent basicity.

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[0/1549 *Received, September 2nd*, 1970]

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[14] J. O'M Bockris, 'Modern Aspects of Electrochemistry,' Butterworths, London, 1954, vol. I, ch. 2.

[15] D. Feakins, 'Physico-Chemical Processes and Mixed Aqueous Solvents,' ed. F. Franks, Heinemann, London, 1967.

[16] F. Franks and D. J. G. Ives, *Quart. Rev.*, 1966, **20**, 1.

[17] O. Popovych, *Critical Rev. Analyt. Chem.*, 1970, **1**, 73.