Standard Potentials of the Silver–Silver Bromide Electrode in Diethylene Glycol–Water Mixtures at Different Temperatures and the Related Thermodynamic Quantities

V. Srinivas Rao and C. Kalidas*
Department of Chemistry, Indian Institute of Technology, Madras 600 036, India

Standard electrode potentials of the silver–silver bromide electrode were determined at five temperatures in the temperature range 5–45 °C in 20, 40, 60, and 80 wt % diethylene glycol–water mixtures by EMF measurements on the cell Pt, H_2(g, 1 atm)|HBr(m), diethylene glycol(X)–water(Y)|AgBr–Ag. The primary medium effects, the mean molal activity coefficients of HBr in the concentration range 0.01–0.08 mol kg^{-1}, and the various thermodynamic parameters for the transfer of HBr from water to these media at 25 °C are also reported. The standard molal potential, ${}_sE^\circ{}_m$, in the various solvent mixtures has been expressed as a function of temperature. The variation of the thermodynamic parameters for the transfer process with solvent composition has been discussed both in terms of the basicity of the solvent mixtures and also their structural effects on the transfer process. The standard molar free energy of transfer, $\Delta G^\circ{}_{t(c)}$, was found to be a linear function of ln ϕ_w (ϕ_w = volume fraction of water) in the various solvent mixtures up to about 60 wt % diethylene glycol and, from the slope, the number of water molecules coordinated to HBr, n, was calculated to be 0.85.

In continuation of our earlier work on this subject (*8*), the present paper deals with the determination of standard potentials of the silver–silver bromide electrode in diethylene glycol–water mixtures of varying composition in order to evaluate the thermodynamics of transfer of hydrogen bromide from water to these solvent mixtures. Although such measurements on galvanic cells involving hydrogen and silver–silver bromide electrodes have been made in a few amphiprotic solvent–water mixtures (*1–3*), no data have so far been reported in diethylene glycol or its aqueous mixtures. As pointed out earlier, such studies not only enable one to develop an understanding of the electrolyte–solvent interactions but under suitable conditions can be utilized for evaluating thermodynamics of ion–solvent interactions by invoking (*10*) suitable extra thermodynamic assumptions. The results on the following cell

$$\text{Pt, H}_2\text{(g, 1 atm)|HBr}(m),\ \text{diethylene glycol}(X)\text{–water}(Y)\text{|AgBr–Ag} \quad (1)$$

in the composition range 20–80 wt % diethylene glycol–water mixtures and in the temperature range 5–45 °C are reported in this work.

Experimental Section

The purification of the solvents and the preparation of the hydrogen and silver–silver bromide electrodes are similar to those described earlier (*7, 8*). Hydrogen bromide was generated by the gradual addition of liquid bromine to tetraline (B.D.H.). The issuing gas was passed through traps containing tetraline to remove the traces of bromine carried along and finally bubbled into the solvent kept in darkness to avoid the effects of light. The preparation and analysis of the acid solutions in the various solvent mixtures are identical with the methods described previously (*8*). The experimental set up and the general procedure used for the EMF measurements are identical with those given earlier (*8*). All measurements were made with a pair of hydrogen electrodes and four Ag–AgBr electrodes. The cells were thermostated at each temperature with an accuracy of ±0.05 °C. The Ag–AgBr electrodes were found to be stable over the entire temperature range, and constancy of the cell EMF to ±0.05 mV over a period of 0.5 h was considered as an adequate criterion of equilibrium in the EMF measurements. The dielectric constants of the aqueous mixtures at various temperatures were determined with a DK 03 dekameter (Wissenschaftliche Technische Werkstatten, West Germany) and have been reported earlier (*8*).

Results and Discussion

The EMF data of the cell (eq 1) in the various solvent mixtures, corrected to a partial pressure of 1 atm of hydrogen, are given in Table I. The standard molal potentials, ${}_sE^\circ{}_m$, of the cell in the various solvent mixtures were determined by extrapolation of the function

$$E^{\circ\prime} = E + 2k \log m - 2kA'm^{1/2}/(1 + aB'm^{1/2}) - 2k \log (1 + 0.002mM_{xy}) = {}_sE^\circ{}_m - 2kbm \quad (2)$$

to zero molality. In the above equation,

$$k = RT \ln 10/F \quad (3)$$

m is the molality of HBr (mol kg^{-1}), A' and B' are the Debye–Huckel (*3*) constants (reported previously (*8*)) on the molality scale, a is the ion size parameter (Å) and b is the coefficient occurring in the expression for activity coefficient as a function of molality, and M_{xy} is the mean molecular weight of the solvent as defined earlier (*8*). In determining ${}_sE^\circ{}_m$, a = 8 Å was used in all solvent compositions as this was found to give good linear plots, with the least slope. Table II gives the ${}_sE^\circ{}_m$ values at all temperatures as also ${}_sE^\circ{}_c$ and ${}_sE^\circ{}_N$, i.e., the ${}_sE^\circ$ values on the molar and mole fraction scale at 25 °C calculated from

$$ {}_sE^\circ{}_c = {}_sE^\circ{}_m + 2k \log d_0 \quad (4)$$

and

$$ {}_sE^\circ{}_N = {}_sE^\circ{}_m - 2k \log (1000/M_{xy}) \quad (5)$$

where d_0 is the density of the solvent. The standard error in $E^\circ{}_m$ is about ±0.25 mV in all the mixtures at different temperatures. The ${}_sE^\circ{}_m$ can be expressed as a function of temperature according to

$$ {}_sE^\circ{}_m = E^\circ{}_{m.25^\circ} + b(t - 25) + c(t - 25)^2 \quad (6)$$

where t is the temperature in degrees celsius and b and c are empirical coefficients. These data are summarized in Table III. The standard deviations in ${}_sE^\circ{}_m$ calculated from eq 6 were found to be within ±0.1 to ±0.2 mV. The stoichiometric mean molal activity coefficients of hydrogen bromide, ${}_s\gamma_\pm$, referred to a value

Table I. EMF Data of Cell (eq 1) (corrected for 1 atm pressure of H_2) from 5 to 45 °C in Volts in Various Diethylene Glycol–Water Mixtures (X = wt % diethylene glycol (g/100 g), m = molality (mol kg^{-1})

	E (V)				
m_{HBr} (mol kg^{-1})	5 °C	15 °C	25 °C	35 °C	45 °C
		$X = 20$			
0.005 43	0.327 19	0.331 52	0.336 82	0.340 78	0.343 84
0.010 56	0.296 54	0.300 16	0.303 12	0.305 52	0.307 37
0.021 61	0.264 99	0.267 77	0.269 74	0.270 99	0.271 73
0.041 59	0.234 51	0.236 71	0.237 55	0.237 35	0.236 93
0.063 36	0.216 48	0.217 91	0.218 50	0.217 92	0.216 18
0.088 30	0.200 70	0.201 27	0.200 56	0.199 38	0.199 25
		$X = 40$			
0.005 95	0.321 06	0.324 86	0.327 83	0.330 31	0.331 74
0.011 91	0.288 76	0.292 12	0.293 16	0.295 39	0.295 36
0.021 73	0.261 70	0.263 28	0.264 13	0.264 39	0.263 67
0.043 55	0.228 92	0.229 90	0.229 54	0.229 16	0.226 99
0.062 97	0.212 79	0.212 96	0.212 36	0.210 62	0.208 51
0.081 83	0.200 17	0.199 84	0.198 63	0.195 07	0.191 61
		$X = 60$			
0.005 82	0.317 07	0.318 23	0.319 09	0.319 03	0.318 79
0.010 78	0.288 75	0.289 00	0.288 86	0.287 60	0.286 18
0.023 20	0.253 45	0.252 57	0.251 08	0.249 17	0.246 92
0.041 76	0.225 17	0.223 12	0.220 82	0.218 36	0.214 77
0.060 29	0.209 42	0.207 72	0.204 72	0.201 15	0.197 59
0.082 73	0.194 72	0.192 24	0.188 81	0.184 39	0.180 76
0.104 60	0.184 87	0.181 99	0.178 18	0.173 00	0.168 24
		$X = 80$			
0.007 02	0.285 52	0.282 36	0.278 44	0.274 17	0.272 37
0.012 16	0.261 65	0.259 51	0.254 75	0.247 67	0.244 53
0.023 35	0.232 10	0.227 57	0.222 64	0.216 13	0.212 28
0.044 73	0.203 60	0.197 96	0.192 77	0.184 60	0.180 46
0.071 96	0.180 62	0.174 97	0.168 88	0.161 04	0.154 79
0.098 90	0.166 85	0.160 79	0.155 25	0.146 71	0.141 82

Table II. ${}_sE^\circ{}_m$ at Different Temperatures and ${}_sE^\circ{}_N$ and ${}_sE^\circ{}_c$ at 25 °C in Volts in Various Diethylene Glycol–Water Mixtures

Diethylene glycol, wt % (g/100 g)	5 °C	15 °C	25 °C	${}_sE^\circ{}_c$	${}_sE^\circ{}_N$	35 °C	45 °C
0[a]	0.079 94	0.075 96	0.071 29	0.071 14	−0.135 11	0.066 04	0.059 97
20	0.072 8	0.068 6	0.064 3	0.065 9	−0.132 8	0.058 5	0.052 2
40	0.070 7	0.065 8	0.059 4	0.062 4	−0.126 3	0.053 0	0.045 2
60	0.064 4	0.056 5	0.048 3	0.052 6	−0.122 7	0.038 5	0.028 5
80	0.039 9	0.028 0	0.014 8	0.019 9	−0.135 5	0.001 0	−0.012 5

[a] See ref 7, p 190.

Table III. Coefficients of the Empirical Equation ${}_sE^\circ{}_m = {}_sE^\circ{}_{m,25^\circ} + b(t - 25) + c(t - 25)^2$

Diethylene glycol wt % (g/100 g)	${}_sE^\circ{}_{m,25^\circ}$	$-b \times 10^4$	$-c \times 10^6$
0	0.071 30	4.955	3.175
20	0.064 1	5.115	3.850
40	0.059 6	6.345	3.850
60	0.048 1	9.058	4.800
80	0.014 9	13.467	4.775

of unity at infinite dilution in the particular solvent and calculated according to the equation

$$\log {}_s\gamma_\pm = ({}_sE^\circ{}_m - E)/2k - \log m \qquad (7)$$

at 25 °C in all the solvent mixtures at rounded molalities of the acid, are recorded in Table IV. The primary medium effects of the hydrogen bromide defined as, $\log {}_m\gamma_\pm$, in the various solvent mixtures at 25 °C calculated from

$$\log {}_m\gamma_\pm = ({}_wE^\circ{}_m - {}_sE^\circ{}_m)/2k \qquad (8)$$

are also recorded in the same table. ${}_wE^\circ{}_m$ and ${}_sE^\circ{}_m$ represent the standard EMF of the cell (eq 1) in water and solvent, respectively. The primary medium effect is a measure of the free energy change associated with the transfer of 1 mol of HBr from water to the given solvent at infinite dilution according to

$$\text{HBr(water)} = \text{HBr(diethylene glycol–water mixture)} \qquad (9)$$

The standard free energy change, $\Delta G^\circ{}_t$, for the process given by eq 9 was calculated on the mole fraction scale for the various solvent mixtures at 25 °C from the expression

$$\Delta G^\circ{}_t = F({}_wE^\circ{}_N - {}_sE^\circ{}_N) \qquad (10)$$

where ${}_wE^\circ{}_N$ and ${}_sE^\circ{}_N$ represent the standard EMF's of the cell (eq 1) on a mole fraction scale. The transfer process (eq 9) is associated with a transfer of charged species, i.e., of H^+ and Br^- ions from water to the mixed solvents at infinite dilution, and it is generally agreed (*4*) that it consists of an electrostatic part, $\Delta G^\circ{}_{t(el)}$, and a nonelectrostatic part, $\Delta G^\circ{}_{t(nonel)}$. While the

Table IV. Mean Molal Activity Coefficient ($_s\gamma_\pm$) at Rounded Molalities and Primary Medium Effects of HBr ($\log {}_m\gamma_\pm$) in Various Diethylene Glycol-Water Mixtures at 25 °C (X, wt % diethylene glycol, g/100 g)

	m_{HBr} (mol kg^{-1})					
X	0.01	0.02	0.04	0.06	0.08	$\log {}_m\gamma_\pm$
20	0.890	0.872	0.850	0.831	0.820	0.058
40	0.880	0.854	0.842	0.820	0.815	0.100
60	0.856	0.832	0.830	0.792	0.780	0.193
80	0.772	0.750	0.710	0.703	0.672	0.475

Table V. Thermodynamic Quantities for Transfer of HBr from Water to Various Diethylene Glycol-Water Mixtures at 25 °C on a Mole Fraction Scale [a]

Diethylene glycol, wt % (g/100 g)	$\Delta G°_t$	$\Delta S°_t$	$\Delta H°_t$
20	−222	1.3	180
40	−849	−6.8	−2 870
60	−1201	−28.2	−9 610
80	42	−62.8	−18 980

[a] $\Delta G°_t$ and $\Delta H°_t$ in J, $\Delta S°_t$ in J K^{-1} mol^{-1}.

electrostatic transfer free energy arises mainly due to the differences in the dielectric constants of the solvents, the nonelectrostatic transfer free energy reflects the contributions of solvation and other specific ion-solvent interactions which depend on the basicity of the solvent. Thus

$$\Delta G°_t = \Delta G°_{t(el)} + \Delta G°_{t(nonel)} \quad (11)$$

The standard entropy of transfer, $\Delta S°_t$, was calculated from

$$\Delta S°_t = (-d/dT)F({}_wE°_N - {}_sE°_N) = F[(b_s - b_w) + 2(c_s - c_w)(t - 25) + (K_w - K_s)] \quad (12)$$

where b_s and c_s and b_w and c_w are the coefficients from Table III in the solvent and water, respectively, and $K_w = 2R/F \ln (1000/18.0154) = (6.92 \times 10^{-4})$ and $K_s = 2R/F \ln (1000/M_{xy})$. The last term of eq 12 arises in the conversion of ${}_sE°_m$ to ${}_sE°_N$. The standard enthalpy of transfer, $\Delta H°_t$, was then calculated from the equation

$$\Delta H°_t = \Delta G°_t + T\Delta S°_t \quad (13)$$

All these thermodynamic quantities are recorded in Table V. The $\Delta G°_t$ values are accurate to ±40 J and the expected errors in $\Delta S°_t$ and $\Delta H°_t$ are ±0.5 J deg^{-1} and ±160 J, respectively. It is seen from this table that $\Delta G°_t$ has small negative values which increase (in the negative direction) up to about 60 wt % diethylene glycol and then attain large positive values after passing through a minimum at this composition. Thus, although, the transfer of HBr from water to diethylene glycol rich media is not spontaneous the process is thermodynamically favorable up to 60 wt % diethylene glycol. The nature of the variation of $\Delta G°_t$ with solvent composition can be qualitatively explained from eq 11 where $\Delta G°_{t(el)}$ becomes more and more positive due to the decreasing dielectric constant of the solvent with increasing additions of diethylene glycol while $\Delta G°_{t(nonel)}$ possibly decreases continuously under the same conditions. This suggests that all diethylene glycol-water mixtures are more basic than water which has recently been established (*11*) on the basis of the ferrocene redox couple reference method in these media. $\Delta H°_t$ (Table V) passes through an endothermic maximum at about 20 wt % diethylene glycol and then becomes increasingly negative up to 80 wt % organic solvent which is similar to the observations (*8*) in the case of HCl in these media. The change in $T\Delta S°_t$ is similar to that in $\Delta H°_t$. According to Franks and Ives (*6*) and Feakins and Voice (*4*), the effect of ionic fields on the structure of the solvent will appear as compensating contributions in $\Delta H°_t$ and $T\Delta S°_t$ and the structural effects of the solvent on the transfer process are revealed through these quantities. The decrease of $\Delta H°_t$ beyond 20 wt % diethylene glycol is associated with a structure making ion-solvent interactions after this composition. However, the endothermic maximum in $\Delta H°_t$ at about 20 wt % diethylene glycol is due to the structure breaking effect of the acid on the ordered structure in solvent mixtures of low diethylene glycol content when the acid is transferred from water to these media. This is because addition of small amounts of alcohols is known (*6*) to promote the hydrogen bonded structure of water and HBr is a better structure breaker in the mixed medium than in water.

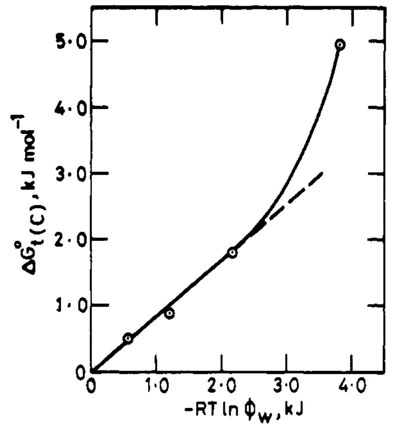

Figure 1. Plot of $\Delta G°_{t(c)}$ against $-RT \ln \phi_w$ at 25 °C.

An examination of $\Delta S°_t$ (Table V) in the presence of increasing amounts of diethylene glycol in general supports the above conclusions. The net structure breaking effect of the ions of the acid at low compositions of the acid is indicated by the positive value of $\Delta S°_t$. At higher compositions of diethylene glycol, $\Delta S°_t$ becomes increasingly negative showing the net structure making effect of the ions which is aided by strong ionic fields in media of low dielectric constant.

A plot of the standard molar free energy of transfer, $\Delta G°_{t(c)}$, against solvent composition in terms of volume fraction of water, ϕ_w, in these media (Figure 1) according to the relation (*5*)

$$\Delta G°_{t(c)} = -nRT \ln \phi_w \quad (14)$$

is fairly linear up to 60 wt % diethylene glycol with $n = 0.85$. This value, representing the number of water molecules coordinated to hydrogen bromide, is less than the values reported (*1, 9*) in other media.

Nomenclature

A', B' = Debye-Huckel constants on molality scale
a = ion size parameter, Å
${}_sE°_m$, ${}_sE°_c$, ${}_sE°_N$ = standard electrode potentials on molality, molarity, and mole fraction scales in solvent, V
${}_wE°_m$, ${}_wE°_c$, ${}_wE°_N$ = standard electrode potentials on molality, molarity, and mole fraction scales in water, V
m = molality of HBr (mol kg^{-1})
k = $RT \ln 10/F$, V
M_{xy} = $100/(X/M_x + Y/M_y)$ Average molecular weight of the solvent (X = wt % diethylene glycol (g/100 g), M_x = molecular weight of diethylene glycol, Y = wt % of water (g/100 g), M_y = molecular weight of water)

$_s\gamma_\pm$ = mean molal activity coefficient of HBr in the solvent referred to solvent standard state

ΔG°_t, ΔH°_t, ΔS°_t = free energies, enthalpies, and entropies of transfer on mole fraction scale, J

$\Delta G^\circ_{t(el)}$ = electrostatic Gibbs free energy of transfer, J

$\Delta G^\circ_{t(nonel)}$ = nonelectrostatic Gibbs free energy of transfer, J

$\Delta G^\circ_{t(c)}$ = standard Gibbs free energy of transfer on molarity scale, J

$\log {}_m\gamma_\pm$ = primary medium effect

ϕ_w = volume fraction of water

$K_s = 2R/F \ln (1000/M_{xy})$

$K_w = 2R/F \ln (1000/18.0154)$

Literature Cited

(1) Banerjee, S. K., Kundu, K. K., Das, M. N., *J. Chem. Soc.*, 161 (1967).
(2) Bax, D., Deligny, C. L., Alfenaar, M., Mohr, W. J., *Recl. Trav. Chim. Pays-Bas.*, **91**, 601 (1972).
(3) Feakins, D., Watson, P., *J. Chem. Soc.*, 4686 (1963).
(4) Feakins, D., Voice, P. J., *J. Chem. Soc., Faraday Trans.*, **68**, 1390 (1972).
(5) Feakins, D., French, C. M., *J. Chem. Soc.*, 2581 (1957).
(6) Franks, F., Ives, D. J. G., *Q. Rev., Chem. Soc.*, **20**, 1 (1966).
(7) Hills, G. J., Ives, D. J. G., "Reference Electrodes", D. J. G. Ives and G. J. Janz, Ed., Academic Press, New York, N.Y., 1961, p 190.
(8) Kalidas, C., Srinivas Rao, V., *J. Chem. Eng. Data*, **19**, 201 (1974).
(9) Mussini, T., Formara, C. M., Andrigo, P., *J. Electroanal. Chem.*, **33**, 189 (1971).
(10) Popovych, O., *Crit. Rev. Anal. Chem.*, **1**, 1 (1970).
(11) Srinivas Rao, V., Kalidas, C., *Indian J. Chem.*, in press.

Received for review September 5, 1975. Accepted February 24, 1976.

Solid + Liquid Phase Equilibria in Binary Mixtures of *N,N*-Dimethylformamide with Halobenzenes

J. F. Moellmer, J. Bevan Ott,* J. Rex Goates, and Dan W. Farrell
Chemistry Department, Brigham Young University, Provo, Utah 84602

Solid–liquid phase diagrams have been obtained from time–temperature cooling and warming curves for the four binary systems formed from *N,N*-dimethylformamide with C_6H_5Cl, C_6H_5Br, *p*-$C_6H_4Cl_2$, and *p*-$C_6H_4Br_2$. All four are simple eutectic systems. The two solid-state phase transitions in *p*-$C_6H_4Cl_2$ were observed, and a solid phase transition at about 194 ± 3 K is reported for *p*-$C_6H_4F_2$.

During the course of a long-range investigation of molecular addition compound formation, the solid–liquid phase diagrams for four binary systems consisting of *N,N*-dimethylformamide (DMF) with C_6H_5Cl, C_6H_5Br, *p*-$C_6H_4Cl_2$, and *p*-$C_6H_4Br_2$ were obtained at 1 atm pressure and over the entire range of composition. These data are reported here. Efforts were made to measure the data with a degree of accuracy that would allow their use in thermodynamic calculations. Combined with other thermal data, they can, for example, be used to calculate activity coefficients (*5*).

Experimental Section

Chemicals. Starting materials were all Aldrich reagent grade. The DMF, C_6H_5Cl, and C_6H_5Br were further purified by distillation in a 100-cm vacuum-jacketed distillation column packed with glass helices and operated at a reflux ratio of 50:1. The center third cut was retained for the experimental measurements. The *p*-$C_6H_4Cl_2$ and *p*-$C_6H_4Br_2$ were purified by melting and recrystallization. The first and last 20% of the sample to crystallize were discarded. Calculations of the change in melting point as a function of the fraction melted showed the following mole percent liquid soluble, but solid insoluble, impurities present: C_6H_5Cl, 0.13; C_6H_5Br, 0.01; *p*-$C_6H_4Cl_2$, 0.06; and *p*-$C_6H_4Br_2$, 0.04. All of the systems except DMF + C_6H_5Br were studied immediately after purification of the DMF with the impurity level in the DMF at 0.04 mol %. The DMF + C_6H_5Br system was studied almost a year later. The C_6H_5Br showed no increase in impurity. However, the impurities in the DMF had increased to 0.22 mol %.

Apparatus, Temperature Scale, and Accuracy of Measurements. The freezing point apparatus has been described previously (*4*). Temperatures were measured with a platinum resistance thermometer which had been calibrated by Leeds and Northrup Co. at the normal boiling temperature of oxygen, the triple point temperature of water, and at the normal melting temperatures of tin and zinc. We checked the calibrations at the beginning and end of the measurements, at the ice point (273.150 K), the mercury freezing point (234.29 K), and the sodium sulfate decahydrate transition temperature (305.534 K). Agreement within 0.01 K between these data and the Leeds and Northrup calibration leads us to believe that our temperature scale is accurate to within ±0.03 K over the temperature range covered.

Melting temperatures were generally obtained from time–temperature warming curves. When supercooling was not excessive, cooling curves were also used. Freezing and melting temperatures generally agreed to within ±0.03 K. The freezing points of the solutions are estimated to be well within 0.1 K.

Samples were prepared by weighing the components to ±0.1 mg. Transfer of chemicals was made with hypodermic syringes to reduce evaporation or contamination of the sample.

Results and Discussion

Table I summarizes the freezing point data for the four systems, and Figures 1–4 are the phase diagrams. The eutectic points are as follows: C_6H_5Cl + DMF, 0.611 mol fraction of DMF and 192.59 K; C_6H_5Br + DMF, 0.690 mol fraction of DMF and 197.82 K; *p*-$C_6H_4Cl_2$ + DMF, 0.966 mol fraction of DMF and 211.28 K; *p*-$C_6H_4Br_2$ + DMF, 0.985 mol fraction of DMF and 212.15 K.

The dotted lines in Figures 1 and 2 are the predicted freezing points assuming ideal solution behavior. The freezing curves for chlorobenzene and bromobenzene were calculated assuming that ΔC_p of fusion is constant with temperature, and, hence, ΔH of fusion varies linearly with temperature. The procedure for making the calculations is described in more detail in an earlier paper (*6*). For DMF, the freezing curves were calculated as-