ELECTROMOTIVE FORCE MEASUREMENTS IN THE SYSTEM $AgNO_3$ AND NaCl IN EQUIMOLAR $NaNO_3$–KNO_3 MIXTURES AND THEIR COMPARISON WITH THE QUASI-LATTICE THEORY

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Electromotive force measurements in dilute solutions of Ag^+ and Cl^- ions in molten equimolar mixtures of $NaNO_3$ and KNO_3 demonstrate over the range of temperatures of 233–528° that the temperature coefficient of the association constant for the formation of the ion pair Ag^+–Cl^- is, within the estimated experimental error, correctly given by the expression $Z(\exp(-\Delta E/RT) - 1)$ which has been derived from the quasi lattice model, where Z is the coördination number and ΔE is the energy of ion pair formation and is a constant. K_1 varies from 1050 (moles/mole solvent)$^{-1}$ at 233° to 133 (moles/mole solvent)$^{-1}$ at 528°. For possible values of Z = 4, 5 and 6 average values of $-\Delta E$ of 5.64, 5.36 and 5.12 kcal./mole, respectively, were calculated.

Introduction

In this paper are described measurements of the activity coefficients of $AgNO_3$ in dilute solutions of Ag^+ and Cl^- ions in molten equimolar mixtures of $NaNO_3$ and KNO_3 at five temperatures ranging from 233 to 528°. In previous papers, similar measurements in pure KNO_3[3,4] and in pure $NaNO_3$[5,6] have been made and compared to the results based on the quasi-lattice model.[6,7] The comparison demonstrated that the temperature coefficient of the association constant K_1, for the formation of the ion pair Ag^+–Cl^- is correctly predicted by the expression derived from the theoretical calculations

$$K_1 = Z(\exp(-\Delta E/RT) - 1) = Z(\beta - 1) \quad (1)$$

where Z is a coördination number, $\beta = \exp(-\Delta E/RT)$, and ΔE is the energy of ion pair formation and is a constant. K_1 was larger and ΔE was more negative by about 1 kcal. in the solvent KNO_3 than in $NaNO_3$. The purpose of this paper is to demonstrate the validity of equation 1 and the constancy of ΔE over a larger range of temperatures than previously and to obtain information on the solvent effect in a mixed solvent.

Experimental

The apparatus, materials and procedure were the same as have been described previously. In some batches of molten reagent grade alkali nitrates a precipitate was observed upon addition of $AgNO_3$. For the experiments particular batches from the manufacturers in which this precipitate was not observed were used. At 233 and 279° it was difficult to fabricate a reference electrode with a high enough conductance which did not leak. Consequently the galvanometer was somewhat sluggish and there was some scatter in the data at these temperatures. At 528° the reproducibility of the measurements was poorer than at the lower temperatures and was about ±1 millivolt.

Results

As described previously,[3,4] electromotive force measurements were made in the concentration cell

$$\mathrm{Ag}\left|\begin{matrix}AgNO_3\\(Na\text{–}K)NO_3\end{matrix}\right\|\begin{matrix}AgNO_3\\NaCl\\(Na\text{–}K)NO_3\end{matrix}\left|\mathrm{Ag}\right.$$

for low concentrations of Ag^+ and Cl^- ions. The addition of increments of NaCl to the right hand half cell at fixed concentrations of $AgNO_3$ in both half cells led to a change of e.m.f. from which the activity coefficient of $AgNO_3$ could be calculated

$$\Delta\text{e.m.f.} \cong \frac{2.303RT}{F} \log \gamma_{AgNO_3} \quad (2)$$

where $a_{AgNO_3} = N_{Ag}N_{NO_3}\gamma_{AgNO_3} \cong R_{AgNO_3}y_{AgNO_3}$ where the N are ion fractions and R_i is the mole ratio of the component i and

$$\frac{R_{AgNO_3}}{N_{Ag}} = 1 + R_{NaCl} + R_{AgNO_3}$$

which is close to unity in dilute solutions so that within the experimental precision, $y_{AgNO_3} = \gamma_{AgNO_3}$. The concentrations of ions for which data are reported are well below concentrations at which a precipitate was observed visually. Values of $-\log \gamma_{AgNO_3}$ are given in Table I for different values of R_{AgNO_3} and R_{NaCl} at 233, 278, 385, 479 and 528°. The experimental results at 385° are plotted in Fig. 1 for $R_{AgNO_3} = 0.2 \times 10^{-3}$ and 2.2×10^{-3}. The comparison in Fig. 1 of the concentration dependence of the experimental results with calculations based on the symmetric and the asymmetric approximations based on the quasi-lattice model indicates that the concentration dependence of the asymmetric approximation is closer to the experimental results. In Fig. 2 are plotted values of $-\log \gamma_{AgNO_3}$ *versus* R_{Cl} at $R_{AgNO_3} \cong 0.2 \times 10^{-3}$ at five temperatures ranging from 233 to 528°. The points at 233 and 278° represent points from four separate sets of measurements, at 385 and 479 from one and at 528 from three. One low set of measurements at 528° which was not plotted was rejected.

Discussion

The solid lines of Fig. 2 represent values of $-\log \gamma$ from the calculations based on the asymmetric approximation[4,5] for the values of Z and ΔE listed in Table II where the range of values of 4 to 6 probably covers all reasonable values of Z. Within the estimated error of the measurements the values of ΔE for any given value of Z are constant at all temperatures at which measurements were made. *This demonstrates that over a*

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(3) M. Blander, F. F. Blankenship and R. F. Newton, *J. Phys. Chem.*, **63**, 1259 (1959).

(4) J. Braunstein and M. Blander, *ibid.*, **64**, 10 (1960).

(5) D. G. Hill, J. Braunstein and M. Blander, *ibid.*, **64**, 1038 (1960).

(6) M. Blander and J. Braunstein, *Ann. N. Y. Acad. Sci.*, **79**, 838 (1960).

(7) M. Blander, *J. Phys. Chem.*, **63**, 1262 (1959).

TABLE I

ACTIVITY COEFFICIENTS CALCULATED FROM E.M.F. CHANGE OF HALF CELLS CONTAINING SOLUTIONS OF $AgNO_3$ IN EQUIMOLAR MIXTURES OF $NaNO_3$ AND KNO_3 UPON ADDITION OF CHLORIDE

Temperature 233°

$R_{AgNO_3} = 0.198 \times 10^{-3}$

$R_{Cl} \times 10^3$	$-\log \gamma_{AgNO_3}$
0.082	0.029
0.185	0.065

$R_{AgNO_3} = 0.200 \times 10^{-3}$

$R_{Cl} \times 10^3$	$-\log \gamma_{AgNO_3}$
0.035	0.011
.080	.023
.170	.063
.200	.087

$R_{AgNO_3} = 0.2014 \times 10^{-3}$

$R_{Cl} \times 10^3$	$-\log \gamma_{AgNO_3}$
0.059	0.025

$R_{AgNO_3} = 0.2014 \times 10^{-3}$

$R_{Cl} \times 10^3$	$-\log \gamma_{AgNO_3}$
0.050	0.017
.087	.029
.141	.058
.193	.078

Temperature 278°

$R_{AgNO_3} = 0.2013 \times 10^{-3}$

$R_{Cl} \times 10^3$	$-\log \gamma_{AgNO_3}$
0.157	0.039
.407	.103
.541	.140
.805	.201
.943	.231
1.154	.288

$R_{AgNO_3} = 0.2003 \times 10^{-3}$

$R_{Cl} \times 10^3$	$-\log \gamma_{AgNO_3}$
0.083	0.016
.313	.072
.614	.142

$R_{AgNO_3} = 0.199 \times 10^{-3}$

$R_{Cl} \times 10^3$	$-\log \gamma_{AgNO_3}$
0.049	0.006
.188	.036
.438	.097
.687	.153
1.068	.237

$R_{AgNO_3} = 0.199 \times 10^{-3}$

$R_{Cl} \times 10^3$	$-\log \gamma_{AgNO_3}$
0.198	0.049
.413	.094
.769	.184
.933	.221
1.177	.276

Temperature 385°

$R_{AgNO_3} = 0.2017 \times 10^{-3}$

$R_{Cl} \times 10^3$	$-\log \gamma_{AgNO_3}$
0.207	0.022
.640	.077
.918	.109
1.174	.138
1.683	.194
2.370	.264
2.946	.320

$R_{AgNO_3} = 2.214 \times 10^{-3}$

$R_{Cl} \times 10^3$	$-\log \gamma_{AgNO_3}$
0.435	0.038
.664	.058
.995	.087
1.303	.115
1.654	.149
1.997	.185

$R_{AgNO_3} = 2.200 \times 10^{-3}$

$R_{Cl} \times 10^3$	$-\log \gamma_{AgNO_3}$
0.270	0.0252
.460	.0443
.725	.0664
1.01	.0909
1.32	.112
1.68	.147

Temperature 479°

$R_{AgNO_3} = 0.2018 \times 10^{-3}$

$R_{Cl} \times 10^3$	$-\log \gamma_{AgNO}$
0.153	0.011
.275	.019
.724	.054
1.008	.070
1.402	.099
1.911	.134
2.227	.155
2.613	.181
2.944	.201

$R_{AgNO_3} = 2.200 \times 10^{-3}$

$R_{Cl} \times 10^3$	$-\log \gamma_{AgNO_3}$
0.188	0.0134
.478	.0302
.722	.0470
1.023	.0665
1.248	.076
1.507	.094
1.857	.117
2.404	.148
3.051	.183

Temperature 528°

$R_{AgNO_3} = 0.2016 \times 10^{-3}$

$R_{Cl} \times 10^3$	$-\log \gamma_{AgNO_3}$
0.333	0.021
.756	.045
1.168	.069
1.614	.093
1.986	.106
2.350	.125
2.809	.150

$R_{AgNO_3} = 0.2015 \times 10^{-3}$

$R_{Cl} \times 10^3$	$-\log \gamma_{AgNO_3}$
0.448[a]	0.023[a]
.0936[a]	.052[a]
1.314[a]	.062[a]
1.918[a]	.089[a]
2.278[a]	.108[a]

$R_{AgNO_3} = 0.1984 \times 10^{-3}$

$R_{Cl} \times 10^3$	$-\log \gamma_{AgNO_3}$
0.528	0.031
1.24	.070
1.95	.108
2.75	.149
3.79	.200
4.68	.242

$R_{AgNO_3} = 0.203 \times 10^{-3}$

$R_{Cl} \times 10^3$	$-\log \gamma_{AgNO_3}$
0.203	0.0069
.437	.0195
.677	.0327
1.03	.0529
1.22	.0641
1.58	.0818
2.15	.1104
2.50	.1290
3.19	.1618

$R_{AgNO_3} = 2.19 \times 10^{-3}$

$R_{Cl} \times 10^3$	$-\log \gamma_{AgNO_3}$
0.254	0.0107
.569	.0264
.774	.0358
1.160	.0546
1.39	.0636
1.70	.0767
1.97	.0906
2.61	.1182
3.11	.1402
4.00	.1820

[a] Rejected.

range of temperatures of 295° and a range of values of K_1 varying by a factor of about eight in this system equation 1 predicts the temperature coefficient of K_1.

The comparison of K_1 and ΔE in the three solvents $NaNO_3$, $NaNO_3$–KNO_3 (50–50 mole %), and

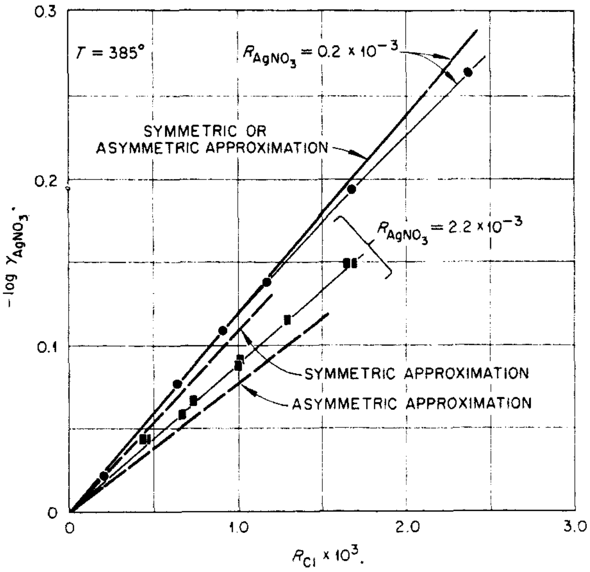

Fig. 1.— − log γ_{AgNO_3} *versus* R_{Cl} at 385° compared with theoretical calculations.

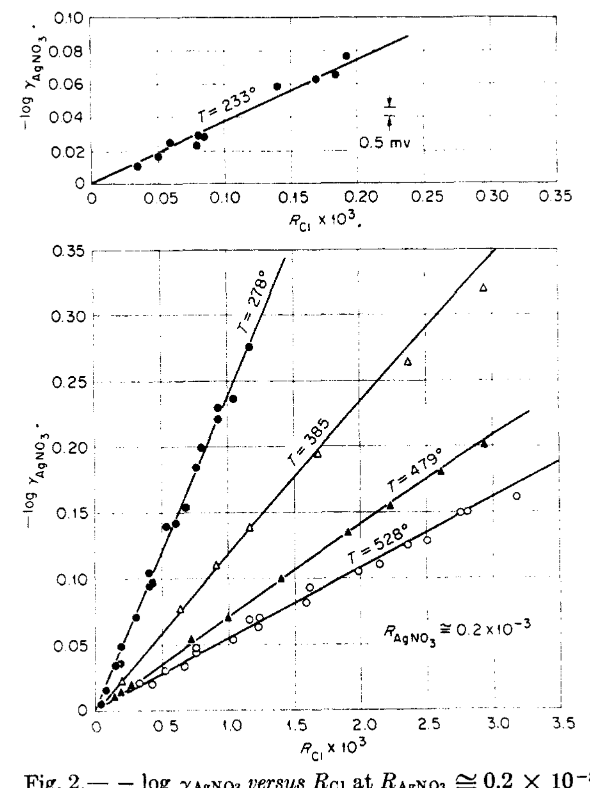

Fig. 2.— − log γ_{AgNO_3} *versus* R_{Cl} at $R_{AgNO_3} \cong 0.2 \times 10^{-3}$ at five temperatures compared with calculations based on the asymmetric approximation.

TABLE II

VALUES OF ΔE AND $Z(\exp(-\Delta E/RT) - 1)$ OBTAINED FROM THE COMPARISON OF THE DATA WITH THE THEORY

T(°K.)	ΔE (kcal.) $Z = 4$	$Z = 5$	$Z = 6$	$K_1 = Z(\beta - 1)$	Estimated error in K_1 (%)
506	5.6	5.4	5.2	1050	±10
551	5.57	5.33	5.13	644	±4
658	5.67	5.38	5.15	302	±3
752	5.72	5.40	5.13	180	±3
801	5.6_2	5.2_8	5.0_0	133	±7

KNO_3 at 385° is made in Table III. The results at other temperatures are comparable. The value

TABLE III

COMPARISON OF THE VALUES OF K_1 AND ΔE IN $NaNO_3$, $NaNO_3$-KNO_3 (50-50 MOLE %), AND KNO_3 AT 385°

		$NaNO_3$	$NaNO_3$-KNO_3 (50-50 mole %)	KNO_3
K_1 (mole/mole KNO_3)$^{-1}$		205	302	455
$-\Delta E$ (kcal./mole)	$Z = 4$	5.17	5.67	6.18
	$Z = 5$	4.88	5.38	5.89
	$Z = 6$	4.65	5.15	5.68

of ΔE in the mixture is the average of the values in the pure $NaNO_3$ and KNO_3 and it appears that for any one value of Z[8]

$$\Delta E_1(NaNO_3\text{-}KNO_3) = N_{Na}\Delta E_1(NaNO_3) + N_K\Delta E_1(KNO_3) \quad (3)$$

The linear relation derived from equations 3 for values of β appreciably greater than unity

$$\ln K_1(NaNO_3\text{-}KNO_3) \cong N_{Na} \ln K_1(NaNO_3) + N_K \ln K_1(KNO_3) \quad (4)$$

is suggested by the results. Equations 3 and 4 are of a type first suggested by Flood and co-workers.[9]

Differences between the solvents $NaNO_3$ and KNO_3 may be ascribed (a) to the differences in the "polarization" of electrons in Ag^+-Cl^- pair "bonds" by the solvent cation[6] or (b) to a coulombic effect, which in a mixture of two cations and two anions of different sizes, aside from contributions due to other types of interactions, will lead to a negative contribution to the energy of association of the small cation with the small anion (*i.e.*, Ag^+ and Cl^- in KNO_3).[10] This negative contribution will be greater for a given small anion and small cation pair the greater the differences in the sizes of the two cations or of the two anions. As both these effects are in the same direction they cannot be separated easily.

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(8) Slightly different values of Z in these two pure molten nitrates should not make any effective difference.

(9) See for example H. Flood, T. Forland and K. Grjotheim, *Z. anorg. u. allgem. Chem.*, **276**, 289 (1954).

(10) If the interionic distance for Ag^+-Cl^- is d_1, for Ag^+-NO_3^- d_2, M^+-Cl d_3, and M^+-NO_3^- d_4 it is easy to demonstrate the well known fact that if $d_3 > d_1$ and $d_4 > d_3$ then the coulombic term $-e^2(1/d_1 + 1/d_4 - 1/d_2 - 1/d_3)$ is negative if the d_i are additive sums of ionic radii so that $d_1 + d_4 = d_2 + d_3$.

SPECTROPHOTOMETRIC DETERMINATION OF THE DISSOCIATION CONSTANT OF SILVER CHLORIDE IN PYRIDINE[1]

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A new spectrophotometric method for the determination of the dissociation constants for equilibria of the type AB $\rightleftarrows$ A + B is described. The method yields $K = 8.4 \times 10^{-6}$ for the dissociation constant of silver chloride in anhydrous pyridine.

Introduction

Although the dissociation constants of approximately thirty compounds have been determined conductometrically[3-5] using pyridine as a solvent, the dissociation constant of silver chloride has not been reported.

A spectrophotometric method has been developed for the determination of the dissociation constant of silver chloride in pyridine and is of interest because of its possible applications to other nonaqueous solvents. Previously described aqueous spectrophotometric methods for the determination of equilibrium constants normally involve media buffered with respect to one of the species produced on dissociation. For example, to determine the dissociation constant of an acid, (1) the pH at which the acid is half neutralized is determined spectrophotometrically,[6] (2) the acid is placed in a buffer of known pH and the ratio of the acid to its conjugate base determined from the known molar absorptivities,[7] (3) the absorbance of the acid in three different buffers is measured and three simultaneous equations are solved to find K,[8] (4) a variation of the Benesi–Hildebrand plot[9] is employed or (5) in salt solutions of constant ionic strength, the Type II plot is used.[10]

Such methods cannot be used in low dielectric constant solvents because of the formation of ion triplets, quadrupoles, etc., and the inability to make suitable estimates of ionic activity coefficients in any but the most dilute of solutions. The method described below is applicable to solutions containing only the solute, AB, which dissociates according to the scheme AB $\rightleftarrows$ A + B, and requires the determination at a suitable wave length of the absorbance as a function of the analytical concentration of AB. The restrictions of the method require

(1) Sponsored by the Office of Ordnance Research, U. S. Army.

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(3) M. M. Davies, *Trans. Faraday Soc.*, **31**, 1561 (1935).

(4) W. F. Luder and C. A. Kraus, *J. Am. Chem. Soc.*, **69**, 2481 (1947).

(5) D. S. Burgess and C. A. Kraus, *ibid.*, **70**, 706 (1948).

(6) N. Bjerrum, *Samm. chem. chemische-tech. Vorträge*, **21**, 30 (1915).

(7) L. Flexser, L. P. Hammett and A. Dingwall, *J. Am. Chem. Soc.*, **57**, 2103 (1935).

(8) D. H. Rosenblatt, *J. Phys. Chem.*, **58**, 40 (1954).

(9) H. A. Benesi and J. H. Hildebrand, *J. Am. Chem. Soc.*, **71**, 2703 (1949).

(10) S. Bruckenstein and D. C. Nelson, *J. Chem. Eng. Data*, in press.