Temperature and concentration dependence of molar electrical conductivity of the ternary system calcium nitrate—potassium nitrate—water

M. SKOKÁNEK and I. SLÁMA

*Institute of Inorganic Chemistry, Czechoslovak Academy of Sciences,
160 00 Prague*

The temperature and concentration dependence of density and electrical conductivity of the system calcium nitrate—potassium nitrate—water was measured in temperature interval from -20 to $+75°C$. Concentration of salts varied in the range 5—27 mole % whilst the ionic fraction of potassium salt acquired values $Z = 0.1, 0.2, 0.3, 0.4$, and 0.5. The experimental values were correlated using a set of empirical equations and also by a single empirical equation describing the temperature and concentration dependence of molar electrical conductivity in the whole studied temperature and concentration range.

Была исследована температурная и концентрационная зависимость молярной электропроводности системы нитрат кальция–нитрат калия––вода в диапазоне температур от -20 до $+75°C$. Интервал концентраций находился от 5 до 27 моль. % солей при ионной доли калиевой соли $Z = 0,1, 0,2, 0,3, 0,4$ и 0.5. Измеренные значения были коррелированы с набором эмпирических уравнений. Было предложено эмпирическое уравнение, хорошо отражающее температурно-концентрационную зависимость молярной электропроводности указанной системы в целом изученном диапазоне температур и концентраций.

By the investigation of metastable substances great attention is paid to the study of their transport properties, which seems to open one of the ways for explanation of their anomalous behaviour. While most of the foregoing works are devoted to the study of binary systems containing water or ternary systems having equimolar ratio of salts the aim of this work is to present a sufficient set of data on molar electrical conductivity of a ternary system at those concentrations where the system is glass-forming. Further, simple semiempirical relationships for the description of temperature and concentration dependence of the molar electrical conductivity were proposed, which allows to estimate its value outside the experimentally studied temperature and concentration range.

Experimental

The samples were prepared in the same way as in previous works [1—3]. Content of potassium and calcium ions is defined by the cationic ratio Z of potassium nitrate which is defined as $Z = n_{K^+}/(n_{K^+} + n_{Ca^{2+}})$, where n_{K^+} and $n_{Ca^{2+}}$ are the amounts of substance of the potassium and calcium ions. The total concentration of salts in solution is expressed in the mole fraction $X = (c_{Ca(NO_3)_2} + n_{KNO_3})/(n_{Ca(NO_3)_2} + n_{KNO_3} + n_{H_2O})$, where $n_{Ca(NO_3)_2}$, n_{KNO_3}, and n_{H_2O} are the corresponding amounts of substance of calcium nitrate, potassium nitrate, and water. Further, mole fractions of calcium nitrate X_1 and of potassium nitrate X_2 are used and it holds $X_1 = (1 - Z)X$ and $X_2 = ZX$.

The electrical conductivity was measured in a glass conductivity cell of volume of 15 cm³ and with separated electrode compartments. The electrode compartments were connected with a thin capillary. Cell constant was 162.256 cm⁻¹. During measurement the cell was immersed in a thermostatic bath the temperature of which was kept with precision ±0.05°C by means of temperature regulator. The measurement of temperature was not carried out at a stationary state but the regulator had been programmed for linear decrease of temperature with the rate 0.6°C/min. Comparison of the electrical conductivity data obtained at stationary state and at programmed decrease of temperature gave a difference not exceeding 0.1%.

Temperature was measured by means of 100 Ω Pt thermometer which was immersed in the thermostatic bath so that it was in contact with the capillary connecting the electrode compartments of the conductance cell. The value of resistivity was measured by a linearized resistivity-voltage convertor the output of which was connected to a digital voltmeter. The apparatus allows reading of temperature with an accuracy ±0.01°C.

The electrolytic conductivity was measured by a modified semiautomatic bridge Tesla BM-484 with digital output and precision 0.05%. All the measurements were carried out at the frequency 1592 Hz.

Pairs of data temperature—conductivity obtained from the voltmeter and bridge were recorded in constant time intervals on paper tape and they were subsequently treated on the computer HP 9830.

Concentration of solutions was determined before and after each measurement undirectly by chelatometric titration of calcium using indicator Kalkon.

The molar electrical conductivity λ $(1/2Ca(NO_3)_2 + KNO_3)$ was calculated from the experimentally obtained specific conductivity $\varkappa/S\ cm^{-1}$ according to the relation

$$\Lambda = \frac{\varkappa (164.09 + 18.0153R - 62.983Z)}{d(2 - Z)} \tag{1}$$

where $d/g\ cm^{-3}$ is the density of the solution at given temperature and composition and $R = (1 - X)/X$. All values of the molar electrical conductivity reported in this paper are in units S cm² mol⁻¹.

For this purpose the experimental values of density [1] were correlated by the relation

$$d = \sum_{i=1}^{3} \left(\sum_{j=1}^{4} A_{ij}X^{j-1} \right) t^{i-1} \tag{2}$$

where A_{ij} are the empirical constants and t is the temperature in °C. The constants of eqn (2) are for given Z presented in Table 1 together with mean relative and maximum relative errors of density.

Results

The molar electrical conductivity of the studied system was investigated in the temperature interval from -20 to $+75$°C. However, the lowest temperature could not be attained in all cases because of crystallization of solutions. The concentration of salts for series of measurements (each of the series having constant Z) ranged approximately from 5 to 25 mole %.

The temperature dependence of the molar electrical conductivity was described by the Fulcher equation

$$\ln \Lambda = A - B/(T - T_0) \qquad (3)$$

where T is the temperature in K and A, B, and T_0 are the constants. The parameter T_0 can be regarded as the temperature at which the ionic mobility of a given solution decreases to the zero value [4]. Constants of the equation together with mean relative errors and confidence limits are for given concentrations presented in Table 2. The confidence limits are calculated at a significance level 0.05.

The concentration dependence of the molar electrical conductivity is described by the equation

$$\ln \Lambda = a + bX + cX^2 + dX^3 \qquad (4)$$

where a, b, c, d are the constants. Before the regression treatment according to eqn (3) the values of molar electrical conductivity were for given temperature calculated using the Fulcher equation (3). The constants of the polynomial (4) are for chosen temperatures and all investigated series summarized in Table 3.

It is evident that the description of the temperature and concentration dependence of the molar electrical conductivity in this way is rather cumbersome and it hardly can be used in praxis because a great number of constants is required. Furthermore, it is difficult to calculate conductivity of solution at arbitrarily chosen temperature and concentration.

For this reason we proposed an equation which would be able with an adequate number of constants to describe the dependence of conductivity of the system on temperature and concentration, even if with worse accuracy.

As a starting point, the Fulcher equation (3) was found to be the most suitable. Assuming that the concentration dependence of constants of the equation would be simple enough the Fulcher equation could be modified for the description of temperature-concentration dependence of molar electrical conductivity.

. *Table 1*

Constants of eqn (2) describing the temperature and concentration dependence of density, $d/\text{g cm}^{-3}$

ij	$Z = 0.1$ A_{ij}	$Z = 0.2$ A_{ij}	$Z = 0.3$ A_{ij}	$Z = 0.4$ A_{ij}	$Z = 0.5$ A_{ij}
11	1.02894089	1.02397085	1.02124509	1.01731630	1.00573074
12	5.73005296	5.52313795	5.12628004	4.96259817	5.00748042
13	−13.63362231	−12.45256813	−10.55928148	−10.25062709	−12.32651272
14	14.66286255	11.98563171	9.10653617	9.23105989	16.29264834
21	$-3.39213153 \times 10^{-4}$	$-3.64770732 \times 10^{-4}$	$-1.90870747 \times 10^{-4}$	$-2.08353562 \times 10^{-4}$	$-4.09779779 \times 10^{-4}$
22	$-8.32803962 \times 10^{-3}$	$-7.13578684 \times 10^{-3}$	$-9.34483591 \times 10^{-3}$	$-9.24753036 \times 10^{-3}$	$-3.96494705 \times 10^{-3}$
23	$3.03295413 \times 10^{-2}$	$2.12712446 \times 10^{-2}$	$4.24250484 \times 10^{-2}$	$3.95217604 \times 10^{-2}$	$5.22038400 \times 10^{-3}$
24	$-2.76909307 \times 10^{-2}$	$-8.62354251 \times 10^{-3}$	$-6.65797986 \times 10^{-2}$	$-6.13977150 \times 10^{-2}$	$-8.20898239 \times 10^{-3}$
31	$-5.95960930 \times 10^{-8}$	$-3.52897314 \times 10^{-6}$	$-3.50860777 \times 10^{-6}$	$-3.65942281 \times 10^{-6}$	$-3.26912384 \times 10^{-6}$
32	$-3.72325241 \times 10^{-5}$	$6.46602745 \times 10^{-5}$	$5.95145029 \times 10^{-5}$	$6.25474634 \times 10^{-5}$	$4.36358214 \times 10^{-5}$
33	$5.34657663 \times 10^{-4}$	$-3.18535336 \times 10^{-4}$	$-3.35906330 \times 10^{-4}$	$-3.25361312 \times 10^{-4}$	$-1.81714468 \times 10^{-4}$
34	$-1.62735629 \times 10^{-3}$	$5.18688030 \times 10^{-4}$	$6.38833183 \times 10^{-4}$	$5.98198328 \times 10^{-4}$	$2.48218593 \times 10^{-4}$
Max. rel. % error	0.1315	0.1467	0.1111	0.1125	0.1078
Mean rel. % error	0.0373	0.0592	0.0420	0.0283	0.0458

M. SKOKÁNEK, I. SLÁMA

Table 2

Constants of eqn (*3*) describing the temperature dependence
of the molar electrical conductivity

X	T_0 K	Confidence limits	A	Confidence limits	$B \cdot 10^{-2}$ K	Confidence limits	Mean rel. error %
			$Z = 0.1$				
0.202	199.9	± 0.2	5.3134	± 0.0147	5.9603	± 3.206	0.080
0.163	188.0	± 0.5	5.3254	± 0.0205	5.3622	± 4.955	0.094
0.145	180.6	± 0.2	5.3980	± 0.0082	5.1570	± 2.128	0.040
0.111	170.5	± 0.4	5.5742	± 0.0114	4.7546	± 3.156	0.040
0.076	162.4	± 0.9	5.8754	± 0.0176	4.3581	± 5.226	0.060
0.052	154.9	± 1.7	6.2153	± 0.0314	4.3307	± 9.772	0.105
			$Z = 0.2$				
0.206	204.5	± 2.7	4.6195	± 0.1229	4.4816	± 25.004	0.924
0.168	184.4	± 0.5	5.3340	± 0.0176	5.0555	± 4.337	0.085
0.145	175.4	± 0.8	5.4799	± 0.0227	4.9637	± 6.002	0.099
0.113	168.2	± 0.4	5.6227	± 0.0111	4.5662	± 3.107	0.047
0.079	161.6	± 0.4	5.9004	± 0.0091	4.2573	± 2.685	0.033
0.053	159.3	± 1.3	6.1984	± 0.0235	4.0355	± 6.999	0.087
			$Z = 0.3$				
0.213	189.2	± 0.9	5.3849	± 0.0543	5.5156	± 10.649	0.712
0.163	177.2	± 2.3	5.3952	± 0.0948	4.7877	± 21.227	0.628
0.140	172.0	± 0.7	5.4855	± 0.0254	4.5760	± 5.927	0.250
0.110	166.1	± 1.3	5.6611	± 0.0383	4.3171	± 9.440	0.331
0.076	162.4	.± 0.7	5.9211	± 0.0185	3.9949	± 4.788	0.122
· 0.052	161.3	± 1.0	6.1915	± 0.0210	3.8032	± 5.640	0.114
			$Z = 0.4$				
0.238	192.2	± 0.9	5.5704	± 0.0528	5.2361	± 10.273	0.642
0.196	182.6	± 1.3	5.5732	± 0.0571	4.8111	± 11.921	0.614
0.166	175.6	± 0.6	5.6452	± 0.0184	4.5727	± 4.140	0.181
0.139	170.6	± 0.7	5.7047	± 0.0217	4.2817	± 5.230	0.180
0.097	163.8	± 0.6	5.9352	± 0.0161	3.9994	± 4.157	0.125
0.075	162.2	± 0.6	6.0951	± 0.0155	3.8473	± 4.018	0.127
0.045	161.4	± 1.2	6.3956	± 0.0256	3.7013	± 6.834	0.183

Table 2 (Continued)

X	T_0 K	Confidence limits	A	Confidence limits	$B \cdot 10^{-2}$ K	Confidence limits	Mean rel. error %
				$Z = 0.5$			
0.248	190.0	± 1.3	5.2064	± 0.0408	4.6184	± 9.807	0.136
0.182	177.9	± 1.7	5.3614	± 0.0435	4.1461	± 11.124	0.199
0.168	174.0	± 1.3	5.4512	± 0.0334	4.1364	± 8.779	0.148
0.135	169.0	± 3.9	5.5967	± 0.0863	3.9211	± 23.072	0.294
0.107	165.4	± 1.3	5.7894	± 0.0279	3.8019	± 7.697	0.147
0.076	160.9	± 1.3	6.0904	± 0.0263	3.8055	± 7.310	0.128
0.051	160.0	± 1.3	6.3670	± 0.0255	3.7522	± 7.029	0.140

Table 3

Constants of eqn (4) describing the concentration dependence
of the molar electrical conductivity

T K	a	b $\cdot 10^{-1}$	c $\cdot 10^{-1}$	d $\cdot 10^{-2}$	Mean rel. error %
		$Z = 0.1$			
258.15*	3.3912	− 2.5906	2.9588	− 4.5626	1.750
268.15*	3.6641	− 2.4538	2.3686	− 3.5410	1.467
278.15	3.9053	− 2.3468	1.9805	− 2.7292	1.236
288.15	4.1193	− 2.2646	1.7584	− 2.0921	1.048
298.15	4.3098	− 2.2028	1.6696	− 1.5998	0.896
308.15	4.4800	− 2.1581	1.6916	− 1.2290	0.775
318.15	4.6326	− 2.1277	1.8037	− 0.9601	0.680
328.15	4.7696	− 2.1092	1.9889	− 0.7764	0.606
338.15	4.8932	− 2.1007	2.2356	− 0.6651	0.551
348.15	5.0048	− 2.1008	2.5319	− 6.1446	0.512
		$Z = 0.2$			
258.15*	3.5057	− 2.8463	8.5529	− 5.1906	0.618
268.15*	3.7764	− 2.6659	7.1751	− 4.1197	0.499
278.15	4.0235	− 2.5527	6.4460	− 3.3661	0.431
288.15	4.2498	− 2.4940	6.2401	− 2.8719	0.404
298.15	4.4578	− 2.4798	6.4605	− 2.5913	0.412
308.15	4.6495	− 2.5017	7.0244	− 2.4859	0.447
318.15	4.8269	− 2.5537	7.8708	− 2.5258	0.504
328.15	4.9913	− 2.6298	8.9425	− 2.6848	0.580
338.15	5.1441	− 2.7258	10.1980	− 2.9423	0.670
348.15	5.2864	− 2.8374	11.5972	− 3.2799	0.771

Table 3 (Continued)

T K	a	b $\cdot 10^{-1}$	c $\cdot 10^{-1}$	d $\cdot 10^{-2}$	Mean rel. error %
			$Z = 0.3$		
258.15	3.5702	− 2.8445	9.3860	− 4.5331	0.626
268.15	3.8363	− 2.6294	7.8497	− 3.5628	0.430
278.15	4.0721	− 2.4680	6.7528	− 2.8217	0.332
288.15	4.2819	− 2.3508	6.0164	− 2.2698	0.261
298.15	4.4693	− 2.2702	5.5768	− 1.8749	0.233
308.15	4.6372	− 2.2200	5.3825	− 1.6104	0.217
318.15	4.7880	− 2.1949	5.3897	− 1.4544	0.206
328.15	4.9241	− 2.1908	5.5633	− 1.3888	0.198
338.15	5.0470	− 2.2040	5.8741	− 1.3985	0.194
348.15	5.1585	− 2.2318	6.2985	− 1.4713	0.192
			$Z = 0.4$		
258.15	3.1938	− 1.2672	− 1.6536	− 1.1804	0.953
268.15	3.5505	− 1.3380	− 0.7396	− 0.9804	0.765
278.15	3.8538	− 1.3910	− 0.0116	− 0.8191	0.624
288.15	4.1120	− 1.4294	0.5614	− 0.6900	0.548
298.15	4.3320	− 1.4555	1.0048	− 0.5876	0.489
308.15	4.5196	− 1.4716	1.3409	− 0.5079	0.430
318.15	4.6794	− 1.4793	1.5863	− 0.4472	0.371
328.15	4.8153	− 1.4801	1.7550	− 0.4024	0.313
338.15	4.9308	− 1.4752	1.8605	− 0.3712	0.301
348.15	5.0286	− 1.4654	1.9109	− 0.3513	0.302
			$Z = 0.5$		
258.15*	3.2000	− 1.1710	− 1.4807	− 0.4497	0.334
268.15*	3.5560	− 1.2553	− 0.5797	− 0.4496	0.279
278.15	3.8609	− 1.3235	0.1641	− 0.4482	0.236
288.15	4.1226	− 1.3785	0.7770	− 0.4460	0.202
298.15	4.3475	− 1.4222	1.2789	− 0.4428	0.175
308.15	4.5410	− 1.4565	1.6869	− 0.4389	0.156
318.15	4.7078	− 1.4830	2.0173	− 0.4347	0.147
328.15	4.8514	− 1.5029	2.2804	− 0.4301	0.142
338.15	4.9750	− 1.5171	2.4866	− 0.4253	0.140
348.15	5.0814	− 1.5264	2.6438	− 0.4201	0.150

* Extrapolation.

As it follows from Table 2, the constant A of the Fulcher equation does depend remarkably on the total concentration of salts. It was found that the most suitable equation for description of concentration dependence of the parameter A is a linear function

$$A = A_1 + A_2 X_1 + A_3 X_2 \qquad (5)$$

where A_1, A_2, and A_3 are the empirical constants.

The constant T_0 from eqn (3) may be considered identical with the temperature of glass transition T_g at infinitely slow rate of cooling. In the previous work [2] it has been found that T_g depends linearly on X_1 and X_2. Therefore we can assume that also concentration dependence of T_0 can be described in this way by the equation

$$T_0 = T_1 + T_2X_1 + T_3X_2 \qquad (6)$$

where T_1, T_2, and T_3 are also the empirical constants.

The concentration dependence of the constant B in the Fulcher equation is somewhat more complicated. After a series of trials it was found that the most suitable in the ternary system calcium nitrate—potassium nitrate—water is the relation

$$B = B_1 + B_2X_1 + B_3X_2 + B_4X_1^2 + B_5X_2^2 + B_6X_1X_2 \qquad (7)$$

where B_1, B_2, B_3, B_4, B_5, and B_6 are the constants.

Substituting the constants expressed in this way into eqn (3) we obtain the final relationship for the description of temperature-concentration dependence of the molar electrical conductivity

$$\ln \Lambda = A_1 + A_2X_1 + A_3X_2 + \frac{B_1 + B_2X_1 + B_3X_2 + B_4X_1^2 + B_5X_2^2 + B_6X_1X_2}{T - T_1 - T_2X_1 - T_3X_2} \qquad (8)$$

Eqn (8) was applied to the treatment of a set of data which consisted of 746 our experimental results to which 461 data obtained for the binary system calcium nitrate—water by *Bressel* [5] were added.

The constants of eqn (8) were calculated using the Gauss—Newton method and subsequently the confidence limits of the parameters were determined. The results are summarized in Table 4 together with the sum of squares of deviations and standard deviations.

Table 4

Constants of eqn (8) describing the temperature-concentration
dependence of the molar electrical conductivity

Parameter	Value of parameter	s_p*	Parameter	Value of parameter	s_p*
A_1	7.2744	0.0466	B_1	−571.0164	11.3960
A_2	−13.4419	0.4530	B_2	50.7424	10.7553
A_3	−5.0839	0.7200	B_3	1250.0761	173.4549
T_1	111.7678	1.1054	B_4	1098.5643	116.1797
T_2	484.5552	7.6184	B_5	143.0508	290.7435
T_3	186.1793	14.7745	B_6	−897.4654	309.6623

* Standard deviation of the parameter.

Discussion

Despite of all objections mentioned above the description of the temperature-concentration dependence of molar electrical conductivity of highly concentrated aqueous solutions by means of eqns (3) and (4) is the most precise which is now at disposal. The maximum relative deviations do not exceed 1% in the case of temperature dependence and 1.5% for the concentration dependence. Accuracy of the description decreases with increasing concentration of salts, and/or Z and with decreasing temperature. This phenomenon is related probably to a change of the structure of solution. Increase of deviations for $Z > 0.3$ can be explained by the fact that for $Z \leq 0.3$ the measurements are carried out in the region of phase diagram where $Ca(NO_3)_2 \cdot 4H_2O$ crystallizes while the other measurements are carried out in region corresponding to crystallization of different forms of KNO_3. One should take also into account the systematic deviations of experimental data from the Fulcher equation which have been discussed earlier [6—8].

Reliability of eqn (8) is supported by a reasonable value of parameter T_0, which is defined by the relation (6), and which is known to be the limit value of the temperature of glass transformation T_g. Usually the calculated T_0 is by 5—20 K lower than T_g. Comparison of the values T_0 calculated according to eqn (8) with the experimentally obtained data of T_g [2, 9, 10] is shown in Fig. 1. It follows that the calculated T_0 are in principle in agreement with the experimental data.

Because the parameter T_1 corresponds to T_0 of pure water it need not be calculated. Unfortunately, literature data are always based on very far extrapolations and fluctuate in the range 130—200 K [11—16]. If we assume that the parameter T_1 is in principle an adjustable one and simultaneously that slopes of
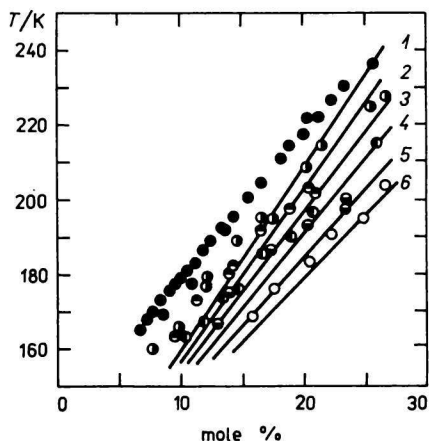

Fig. 1. Comparison of the experimental T_g and calculated T_0 (full lines) temperatures of glass transition.
1. ● $Z = 0.0$; 2. ◑ $Z = 0.1$; 3. ◕ $Z = 0.2$; 4. ◐ $Z = 0.3$; 5. ◔ $Z = 0.4$; 6. ○ $Z = 0.5$.

temperature dependences of T_0 and T_g should be approximately the same we obtain for water as the most probable value of T_0 the value 120—125 K. It was verified by calculation that the choice of T_1 in new optimization of the rest 11 parameters does not practically influence the accuracy of the description of temperature dependence. For $T_1 = 111.77$ the standard deviation equals 6.19×10^{-2} and for $T_1 = 120.00$ it equals 6.33×10^{-2}.

Comparison of calculated molar electrical conductivities for the case of infinite dilution and for molten salts with literature data shows no great discrepancy, which supports the assumption that the proposed equation is suitable also for estimation of electrical conductivity outside investigated temperature and concentration range.

References

1. Skokánek, M., *CSc. Thesis.* Institute of Inorganic Chemistry, Czechoslovak Academy of Sciences, Prague, 1979.
2. Skokánek, M., Malá, J., and Sláma, I., *Collect. Czech. Chem. Commun.,* in press.
3. Skokánek, M. and Sláma, I., *Collect. Czech. Chem. Commun.,* in press.
4. Cohen, H. and Turnbull, D., *J. Chem. Phys. 31,* 1164 (1969).
5. Bressel, R. D., *Thesis.* Purdue University, Lafayette, Indiana, 1970.
6. Tweer, H., Laberge, N., and Macedo, P. B., *J. Amer. Ceram. Soc. 54,* 121 (1971).
7. Bose, R., Weiller, R., and Macedo, P. B., *Phys. Chem. Glasses 11,* 117 (1970).
8. Weiller, R., Blaser, S., and Macedo, P. B., *J. Phys. Chem. 73,* 4147 (1969).
9. Malá, J. and Sláma, I., *Collect. Czech. Chem. Commun.,* in press.
10. Sare, E. J., *Thesis.* Purdue University, Lafayette, Indiana, 1971.
11. Dietzel, A. and Pogel, M. J., *Proceedings of the 3rd International Glass Congress,* p. 219. Venice, 1953.
12. Miller, A. A., *Science 163,* 1325 (1968).
13. Sare, E. J. and Angell, C. A., *J. Solid State Chem. 2,* 53 (1973).
14. Bernini, V., Fittipaldi, F., and Ragozzino, E., *Nature* (London) *224,* 910 (1969).
15. Korsin, L., Drost-Hansen, W., and Millero, F. J., *J. Phys. Chem. 73,* 34 (1969).
16. Miller, A. A., *J. Chem. Phys. 38,* 1568 (1963).

Translated by P. Fellner