

Conductance of Electrolytes in 1-Propanol Solutions from -40 to 25 °C

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Conductance data for solutions of LiCl, NaBr, NaI, KI, KSCN, RbI, Et₄NI, Pr₄NI, Bu₄NI, Bu₄NClO₄, n-Am₄NI, i-Am₄NI, n-Hept₄NI, Me₂Bu₂NI, MeBu₃NI, EtBu₃NI, i-Am₃BuNI, and i-Am₃BuNBPh₄ in 1-propanol at -40, -30, -20, -10, 0, 10, and 25 °C are communicated and discussed. Evaluation of the data is performed on the basis of a conductance equation that includes a term in $c^{3/2}$. Single ion conductances at 25 and 10 °C are determined with the help of transference numbers t_o^+ (KSCN/PrOH); the data are compared to data estimated by other methods. Ion-pair association constants and their temperature dependence are discussed in terms of contact and solvent separated ion pairs, and the role of non-coulombic forces is shown with the help of an appropriate splitting of the Gibbs energy of ion-pair formation.

KEY WORDS: Electrolyte conductance; single ion conductance; ion-pair formation; non-coulombic interactions; 1-propanol solutions; alkali metal salts; tetraalkylammonium salts.

1. INTRODUCTION

The temperature dependences of conductance and transference numbers of electrolytes in nonaqueous solutions are the subject of a comprehensive study in our laboratory aimed at an understanding of ion-ion and ion-solvent interactions in these solutions. This paper continues the study on alcohol solutions that began with ethanol solutions.⁽¹⁾ Transference numbers are given in Ref. 2.

For the standard methods of measurement and data analysis, which is based on the chemical model (CM) of electrolyte solutions including short range interactions,^(3,4) the reader is referred to Refs. 1

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and 2. Conductance data were analyzed with the help of the series-developed Fuoss-Hsia equation (coefficients in Ref. 5), which was adapted to the CM by appropriate distance parameters R .

$$\Lambda = \alpha [\Lambda_0 - S(\alpha c)^{1/2} + E' \alpha c \ln \alpha c + J_1(R) \alpha c + J_2(R) (\alpha c)^{3/2}] \quad (1a)$$

$$\frac{1 - \alpha}{\alpha^2 c} = K_A y_{\pm}'^2; \quad y_{\pm}' = \exp \left[- \frac{\kappa q}{1 + \kappa R} \right] \quad (1b \text{ and } c)$$

In Eqs. (1), Λ is the molar conductance at molar concentration c , and Λ_0 is its limiting value; $(1 - \alpha)$ is the fraction of oppositely charged ions acting as ion pairs; K_A is the thermodynamic association constant, and y_{\pm}' is the activity coefficient of the dissociated fraction of the electrolyte; R is the distance up to which oppositely charged ions are considered to be ion pairs. The quantities q and κ are given by (cgs units)

$$q = e^2/2\epsilon kT; \quad \kappa^2 = 16 \times 10^{-3} \pi q N_A \alpha c \quad (2a \text{ and } b)$$

The symbols of Eqs. (2) have their usual meaning; e is the elementary charge, ϵ is the relative permittivity of the solvent, N_A is Avogadro's number, k is the Boltzmann constant, and T is the Kelvin temperature.

Data analysis commonly is based on the use of independent distance parameters $R = R(y_{\pm}')$, $R_1 = R(J_1)$, and $R_2 = R(J_2)$ to yield four, three, and two parameter fits.^(1,5) In this paper, we used three parameter fits for which R_1 was fixed to R ; the final values of Λ_0 , K_A , and R_2 were obtained by nonlinear least squares iteration.⁽¹⁾ Only the solutions of *i*-Am₃BuNBPh₄ required a two parameter fit, $R_2 = R_1 = R$, as a consequence of limited solubility ranges.

As usual in CM calculations, the upper distance R of ion-pair formation for alkali metal and tetraalkylammonium salts in alcohol solutions was fixed to the sum of closest ion approach, a or a' , and the dimension of an orientated solvent molecule (1-propanol, $s = 6.9$ Å).⁽¹⁾ The distance of closest approach a for the tetraalkylammonium, cesium, rubidium, and potassium salts is the contact distance of cation and anion, $a = a_+ + a_-$. The data from lithium and sodium salt solutions were analyzed by fixing the distance of closest approach to $a' = a + d_{OH}$, *i.e.*, when assuming that the mutual distance of cation and anion includes at least one OH-length ($d_{OH} = 2.8$ Å), and a solvent separated ion pair is formed. When analyzed with the help of $a = a_+ + a_-$, the data from lithium and sodium salts exhibit the same inconsistencies within the pattern of enthalpies and entropies of association

Table I. Experimental Results from Solvent Property Determinations and Conductance Measurements on Various Salts

	25°C	10°C	0°C	-10°C	-20°C	-30°C	-40°C
Solvent Properties							
d	0.79954	0.81150	0.81941	0.82728	0.83513	0.84299	0.85090
ϵ	20.436	22.567	24.093	25.711	27.430	29.258	31.205
η	1.967	2.840	3.710	4.947	6.748	9.442	13.600
$\tilde{m} \times 10^4$	Molar Conductances, Λ						
LiCl: $a = 2.59$; $D = 0.036$; $M_E = 42.39$							
3.1481	17.804	12.299	9.3909	7.0333	5.1547	3.6866	2.5617
8.7980	16.152	11.347	8.7358	6.5845	4.8502	3.4834	2.4279
16.9269	14.732	10.502	8.1467	6.1783	4.5740	3.2978	2.3058
23.3535	13.948	10.023	7.8083	5.9427	4.4127	3.1894	2.2343
30.4632	13.267	9.5992	7.5072	5.7314	4.2671	3.0909	2.1690
37.3280	12.740	9.2647	7.2682	5.5631	4.1496	3.0107	2.1162
44.8130	12.248	8.9504	7.0396	5.4011	4.0371	2.9341	2.0647
53.6691	11.765	8.6375	6.8109	5.2372	3.9224	2.8555	2.0124
NaBr: $a = 2.94$; $D = 0.084$; $M_E = 102.89$							
2.5839	20.475	14.188	10.863	8.1582	5.9985	4.3040	2.9967
8.2454	18.478	13.030	10.062	7.6075	5.6223	4.0514	2.8294
11.6916	17.697	12.565	9.7379	7.3831	5.4682	3.9467	2.7605
15.6290	16.970	12.128	9.4307	7.1689	5.3219	3.8475	2.6952
19.4843	16.385	11.770	9.1770	6.9912	5.1987	3.7651	2.6370
25.7675	15.607	11.289	8.8328	6.7504	5.0332	3.6515	2.5646
35.2604	14.703	10.717	8.4217	6.4593	4.8297	3.5128	2.4722
46.7632	13.871	10.179	8.0319	6.1807	4.6345	3.3786	2.3820
59.5087	13.161	9.7152	7.6908	5.9343	4.4605	3.2586	2.3014
NaI: $a = 3.18$; $D = 0.112$; $M_E = 149.89$							
1.8578	22.677	15.674	12.008	9.0328	6.6543	4.7910	3.3470
3.9685	21.795	15.150	11.636	8.7716	6.4750	4.6659	3.2637
7.5119	20.784	14.563	11.208	8.4704	6.2655	4.5232	3.1684
10.7557	20.079	14.116	10.905	8.2590	6.1179	4.4227	3.1004
15.0183	19.348	13.672	10.588	8.0328	5.9619	4.3145	3.0286
21.0104	18.537	13.170	10.229	7.7798	5.7856	4.1937	2.9474
29.3884	17.675	12.629	9.8409	7.5032	5.5916	4.0601	2.8577
39.5618	16.862	12.119	9.4694	7.2379	5.4043	3.9314	2.7703
KI: $a = 3.53$; $D = 0.127$; $M_E = 166.01$							
2.1970	23.753	16.516	12.681	9.5493	7.0386	5.0639	3.5349
6.0539	21.883	15.426	11.926	9.0320	6.6898	4.8318	3.3838
8.4060	21.056	14.932	11.581	8.7935	6.5275	4.7231	3.3131
11.4719	20.226	14.429	11.227	8.5484	6.3595	4.6112	3.2412
15.7321	19.280	13.848	10.816	8.2611	6.1627	4.4792	3.1536
20.3205	18.480	13.346	10.455	8.0078	5.9887	4.3611	3.0763

Table I. Continued

$\bar{m} \times 10^4$	25°C	10°C	0°C	-10°C	-20°C	-30°C	-40°C
KSCN: a = 4.73; D = 0.054; $M_E = 97.18$							
4.4455	23.078	16.185	12.483	9.4363	6.9740	5.0278	3.5155
10.1738	21.094	14.995	11.650	8.8589	6.5829	4.7660	3.3445
13.8290	20.211	14.455	11.266	8.5923	6.3989	4.6433	3.2647
18.9785	19.230	13.844	10.829	8.2858	6.1894	4.5021	3.1723
26.7622	18.108	13.133	10.317	7.9225	5.9383	4.3320	3.0601
36.8051	17.031	12.437	9.8094	7.5609	5.6854	4.1598	2.9463
52.4104	15.824	11.641	9.2226	7.1386	5.3883	3.9557	2.8098
RbI: a = 3.69; D = 0.14; $M_E = 212.37$							
1.0168	24.945	17.312	13.286	10.004	7.3785	5.3122	3.7099
2.2007	23.959	16.749	12.901	9.7440	7.2024	5.1946	3.6358
4.8016	22.354	15.797	12.237	9.2865	6.8944	4.9904	3.5025
6.4090	21.614	15.351	11.923	9.0694	6.7455	4.8916	3.4383
10.8867	20.051	14.391	11.243	8.5945	6.4198	4.6721	3.2953
20.7499	17.869	13.003	10.237	7.8805	5.9229	4.3348	3.0718
Et ₄ NI: a = 6.20; D = 0.09; $M_E = 257.16$							
0.8228	27.343	18.931	14.517	10.925	8.0491	5.7804	4.0376
1.5645	26.487	18.378	14.101	10.615	7.8232	5.6249	3.9217
1.7803	26.271	18.232	13.990	10.532	7.7595	5.5775	3.8871
2.7900	25.390	17.647	13.552	10.205	7.5184	5.4016	3.7606
3.2998	24.986	17.381	13.350	10.053	7.4052	5.3179	3.7013
4.5188	24.162	16.832	12.833	9.7400	7.1723	5.1487	3.5787
4.5974	24.120	16.804	12.913	9.7239	7.1619	5.1414	3.5738
6.2022	23.266	16.202	12.455	9.3793	6.9052	4.9524	3.1486
7.4359	22.642	15.807	12.154	9.1528	6.7367	4.8301	-
8.8666	22.042	15.396	11.846	8.9193	6.5631	4.7036	-
10.8742	21.305	14.903	11.464	8.6331	6.3511	4.5480	-
16.3348	19.766	13.845	10.654	-	-	-	-
Pr ₄ NI: a = 6.72; D = 0.09; $M_E = 313.26$							
0.9616	24.647	17.002	13.000	9.7515	7.1617	5.1308	3.5655
3.0560	22.873	15.831	12.116	9.0900	6.6726	4.7744	3.3095
6.2588	21.124	14.663	11.226	8.4222	6.1759	4.4112	3.0494
9.6401	19.910	13.834	10.596	7.9457	5.8204	4.1511	2.8639
13.5497	18.734	13.031	9.9818	7.4807	5.4745	3.8983	2.6846
21.1079	17.177	11.961	9.1587	6.8570	5.0108	3.5603	2.4441
29.1517	16.003	11.147	8.5381	6.3852	4.6603	3.3044	2.2628
45.3120	14.387	10.024	7.6682	5.7292	4.1726	2.9504	2.0134
Bu ₄ NI: a = 7.14; D = 0.098; $M_E = 369.37$							
0.6341	23.483	16.191	12.377	9.2851	6.8204	4.8902	3.4011
2.1689	22.023	15.221	11.644	8.7415	6.4172	4.5975	3.1926
3.8748	20.899	14.470	11.075	8.3134	6.1001	4.3640	3.0264
5.8355	19.983	13.852	10.607	7.9580	5.8370	4.1724	2.8876
8.8584	18.793	13.046	9.9902	7.4932	5.4908	3.9190	2.7070
11.4259	18.011	12.510	9.5794	7.1828	5.2587	3.7492	2.5858
14.2793	17.290	12.015	9.1989	6.8945	5.0452	3.5925	2.4756
20.7188	16.036	-	8.5358	6.3882	4.6696	3.3184	2.2792

Table I. Continued

$\bar{m} \times 10^4$	25°C	10°C	0°C	-10°C	-20°C	-30°C	-40°C
Bu ₄ NC10 ₄ : a = 7.34; D = 0.070; M _E = 341.92							
1.0451	24.812	17.238	13.243	9.9820	7.3631	5.2968	3.6920
3.2859	22.243	15.452	11.846	8.9003	6.5334	4.6671	3.2263
6.6078	19.963	13.852	10.597	7.9352	5.7988	4.1184	2.8264
13.4805	17.221	11.923	9.0942	6.7796	4.9261	3.4740	2.3639
19.2582	15.778	10.906	8.3023	6.1740	4.4716	3.1415	2.2177
26.3861	14.503	10.006	7.6036	5.6400	4.0721	2.8503	1.9221
36.0952	13.256	9.1281	6.9209	5.1201	3.6843	2.5692	1.7245
48.1253	12.149	8.3461	6.3149	4.6588	3.3424	2.3212	1.5511
n-Am ₄ NI: a = 7.45; D = 0.108; M _E = 425.48							
1.0627	21.895	15.113	11.566	8.6873	6.3884	4.5842	3.1905
2.6433	20.635	14.271	10.924	8.2029	6.0275	4.3203	3.0017
4.2625	19.682	13.629	10.438	7.8364	5.7549	4.1204	2.8582
7.4003	18.326	12.711	9.7348	7.3045	5.3584	4.8304	2.6487
11.6967	17.012	11.813	9.0470	6.7835	4.9694	3.5448	2.4459
15.7414	16.088	11.177	8.5589	6.4137	4.6938	3.3431	2.3026
22.3888	14.942	10.386	7.9490	5.9513	4.3490	3.0923	2.1237
28.1478	14.180	9.8489	7.5423	5.6427	4.1191	2.9238	2.0050
42.6708	12.793	8.8901	6.7959	5.0763	3.6974	2.6173	1.7886
i-Am ₄ NI: a = 7.20; D = 0.108; M _E = 425.48							
1.0611	22.082	15.224	11.640	8.7324	6.4153	4.5978	3.1965
2.3214	20.994	14.502	11.092	8.3200	6.1079	4.3721	3.0340
4.0337	19.896	13.760	10.527	7.8939	5.7903	4.1397	2.8668
8.1122	18.089	12.533	9.5874	7.1837	5.2607	3.7513	2.5894
11.6160	17.006	11.789	9.0174	6.7519	4.9385	3.5161	2.4214
16.3008	15.913	11.036	8.4371	6.3124	4.6105	3.2765	2.2516
24.3953	14.551	10.094	7.7114	5.7616	4.2001	2.9781	2.0404
31.6968	13.655	9.4711	7.2316	5.3987	3.9301	2.7817	1.9023
40.2314	12.847	8.9046	6.7950	5.0666	3.6841	2.6031	1.7764
n-Hept ₄ NI: a = 8.08; D = 0.119; M _E = 537.69							
0.4359	21.132	14.567	11.135	8.3603	6.1420	4.4012	3.0505
1.2965	20.279	14.013	10.730	8.0617	5.9326	4.2585	2.9625
2.7010	19.297	13.361	10.237	7.6944	5.6595	4.0605	2.8233
4.2704	18.438	12.785	9.7997	7.3648	5.4168	3.8834	2.6964
6.2239	17.594	12.213	9.3633	7.0366	5.1721	3.7057	2.5691
9.4560	16.520	11.481	8.8032	6.6124	4.8550	3.4724	2.4038
15.8444	15.029	10.457	8.0167	6.0153	4.4091	3.1462	2.1726
21.2223	14.129	9.8341	7.5364	5.6526	4.1388	2.9489	2.0315
MeBu ₃ NI: a = 5.67; D = 0.107; M _E = 327.29							
1.6749	22.956	15.872	12.144	9.1204	6.7003	4.8025	3.3372
3.5208	21.502	14.905	11.416	8.5698	6.2945	4.5050	3.1224
6.5575	19.845	13.793	10.571	7.9365	5.8231	4.1600	2.8753
10.7098	18.299	12.744	9.7701	7.3313	5.3724	3.8311	2.6417
15.2903	17.081	11.906	9.1286	6.8466	5.0119	3.5682	2.4551
20.4845	16.034	11.187	8.5775	6.4293	4.7011	3.3426	2.2945
26.2046	15.145	10.569	8.1023	6.0690	4.4336	3.1475	2.1570
32.7629	14.333	10.008	7.6687	5.7408	4.1898	2.9703	2.0320

Table I. Continued

$\bar{m} \times 10^4$	25°C	10°C	0°C	-10°C	-20°C	-30°C	-40°C
Me ₂ Bu ₂ Ni: a = 5.67; D = 0.102; M _E = 285.21							
0.9751	24.663	17.037	13.043	9.7927	7.2003	5.1617	3.5885
1.8572	23.667	16.392	12.557	9.4326	6.9349	4.9714	3.4528
3.4684	22.308	15.491	11.878	8.9252	6.5591	4.6968	3.2568
7.2456	20.166	14.057	10.785	8.1043	5.9528	4.2522	2.9407
11.5838	18.545	12.955	9.9477	7.4727	5.4808	3.9106	2.6968
18.4793	16.816	11.768	9.0393	6.7869	4.9705	3.5390	2.4330
27.8712	15.252	10.687	8.2079	6.1583	4.5040	3.1994	2.1931
42.8443	13.639	9.5634	7.3417	5.5012	4.0162	2.8454	1.9440
59.5677	12.445	8.7255	6.6936	5.0107	3.6514	2.5811	1.7582
EtBu ₃ Ni: a = 6.20; D = 0.108; M _E = 341.32							
0.9995	23.860	16.460	12.584	9.4349	6.9247	4.9577	3.4345
2.7875	22.296	15.437	11.818	8.8684	6.5100	4.6574	3.2272
6.7490	20.164	13.998	10.727	8.0437	5.9046	4.2166	2.9140
10.1079	18.947	13.177	10.097	7.5752	5.5526	3.9600	2.7309
14.3815	17.790	12.383	9.4904	7.1156	5.2104	3.7118	2.5563
20.4521	16.568	11.542	8.8424	6.6241	4.8459	3.4475	2.3682
25.9872	15.717	10.954	8.3903	6.2821	4.5924	3.2614	2.2358
36.7183	14.483	10.092	7.7264	5.7792	4.2179	2.9891	2.0448
46.3447	13.651	9.5135	7.2807	5.4407	3.9657	2.8073	1.9164
i-Am ₃ BuNi: a = 7.18; D = 0.113; M _E = 411.46							
1.3570	22.110	15.248	11.658	8.7437	6.4206	4.5997	3.1935
2.8657	20.903	14.449	11.049	8.2871	6.0813	4.3520	3.0169
5.9712	19.227	13.313	10.185	7.6353	5.5966	3.9965	2.7628
11.1664	17.423	12.081	9.2424	6.9221	5.0645	3.6081	2.4858
19.6208	15.580	10.814	8.2688	6.1849	4.5158	3.2072	2.2016
29.8653	14.149	9.8179	7.5005	5.6029	4.0828	2.8924	1.9790
40.4734	13.105	9.0919	6.9412	5.1781	3.7669	2.6631	1.8180
50.8879	12.333	8.5507	6.5232	4.8620	3.5322	2.4930	1.6983
i-Am ₃ BuNBPh ₄ : a = 9.74; D = 0.16; M _E = 603.79							
0.10852	20.670	14.248	10.885	8.1451	5.9475	4.2301	2.9061
0.38967	20.159	13.879	10.581	7.9050	5.7612	4.0866	2.7943
0.53759	20.090	13.813	10.526	7.8424	5.7179	4.0494	2.7641
0.71074	19.901	13.668	10.408	7.7558	5.6389	3.9880	2.7153
0.91637	19.625	13.471	10.247	7.6278	5.5384	3.9099	2.6576
1.0871	19.461	13.353	10.145	7.5450	5.4723	3.8584	2.6174
1.3040	19.233	13.177	10.007	7.4307	5.3840	3.7907	2.5677
1.5265	19.020	13.016	9.8759	7.3283	5.3021	3.7282	-

^aUnits: density d , g-cm⁻³; permittivity ϵ , no; viscosity η , cP; molonity \bar{m} , mol-(kg of solution)⁻¹; molar conductance Λ , S-cm²-mol⁻¹; distance parameter a , Å; density gradient D , g-cm⁻³-(mol-kg⁻¹)⁻¹; molar mass M_E , g-mol⁻¹; blanks, solubility limit is surpassed.

which were observed for these salts in ethanol solutions. The values for the a -parameters⁽⁴⁾ are quoted in Table I.

2. EXPERIMENTAL

2.1. Materials

1-Propanol (p.A. Merck) was dried with amalgamated aluminum shot;⁽⁶⁾ ammonia and amines were removed by boiling for twelve hours in the presence of sulfanilic acid. Subsequent distillation over a packed column (about 50 plates)⁽⁷⁾ reduced the water content to less than 10 ppm and the specific conductance to less than 10^{-9} S-cm⁻¹. All operations and the storage of the final product were carried out under purified argon.

The temperature dependent permittivities ϵ , viscosities η , and densities d of 1-propanol determined by the usual methods of our laboratory⁽⁷⁾ are compiled in Table I.

Preparation and/or purification of NaI, KI, KSCN, Pr₄NI, *i*-Am₃BuNI, and *i*-Am₃BuNBPh₄ is described in Ref. 1, and of Bu₄NI and Bu₄NCIO₄ in Ref. 8.

RbI (Merck suprapur) and NaBr (Merck suprapur) were purified like NaI. Pure LiCl was prepared by reaction of Li (Ventron, 99.95%) with HCl (Merck, p.a.). The reaction product was dissolved at 70 °C in fuming hydrochloric acid (Merck, p.a.) and precipitated from this solution at -20 °C. After repeated recrystallization (5 times), LiCl was ground in an argon atmosphere, slowly heated to 500 °C in a quartz tube furnace under a streaming mixture of pure argon and HCl; from 500 °C to the melting point of LiCl, the sample was heated under highly pure HCl; cooling down was carried out under increasing argon content of the gas mixture. The final product was stored under pure argon.

Et₄NI (K&K Laboratories) was recrystallized four times from methanol-diethyl ether mixtures and dried like Bu₄NI.⁽⁸⁾ *n*-Am₄NI (Eastman Kodak), *i*-Am₄NI (Eastman Kodak), and *n*-Hept₄NI (Serva) were five times recrystallized from acetone-diethyl ether mixtures at -20 °C and dried at 50 to 60 °C and 10⁻³ mbar in the presence of SICAPENT (Merck). Bu₃MeNI, Bu₃EtNI, and Me₂Bu₂NI were prepared by reaction of the corresponding amines and alkyl iodides: Bu₃N + MeI (water bath, 90 °C); Bu₃N + EtI (water bath, 90 °C); MeBu₂N + MeI (70 °C) (initial products (Fluka), except MeBu₂N (K&K Laboratories)). The reaction products were dissolved in

ethanol, precipitated by addition of diethyl ether, and repeatedly recrystallized from acetone-diethyl ether mixtures at low temperatures. The purity of the final products was checked by elementary analysis and by their melting points. All operations and the final storage of the purified products under pure argon were carried out with exclusion of light.

The density gradient D for each salt in 1-propanol, needed for the conversion of molonities \bar{m} [mol-(kg of solution)⁻¹] to molarities c [mol-dm⁻³]

$$c = \bar{m}d_{\text{soln}}(T); \quad d_{\text{soln}}(T) = d(T) + D\bar{m} \quad (3a \text{ and } b)$$

was determined with the help of a Paar densimeter (DMA 60, DMA 601 HT), see Ref. 1. In Eqs. (3), $d_{\text{soln}}(T)$ and $d(T)$ are the densities of the solution and the pure solvent at temperature T . The density gradients D were found to be independent of temperature.

The density gradients D and the molar masses M_E of all salts are compiled in Table I.

2.2. Conductance Measurements

The conductance measurements were carried out at each molonity under purified argon in temperature cycles through all temperatures of the program, beginning and ending at 25 °C; the Λ - c - T diagrams were established by the method given in Refs. 1 and 9. The calibration of the three-electrode conductance cells is based on the temperature dependence of aqueous potassium chloride solutions yielding linear equations of the cell constants vs. temperature.⁽⁹⁾ The measured molonities (accuracy: 0.01-0.02%) and molar conductances (accuracy: 0.01-0.02%) are compiled in Table I.

3. DISCUSSION

The results of the three ($R = R_1$) and two parameter ($R = R_1 = R_2$, only i -Am₃BuNBPh₄) fits are reported in Tables III and V. The distance parameters R_2 from three parameter fits are not relevant for further discussion. Suffice it to mention that R_2 is found independent of temperature and in agreement with R , thus demonstrating the reliability of the method.

A comparative study of two, three, and four parameter fits for various conductance equations and various assumptions on the choice of R can be found in Ref. 7; data analysis for some propanol solutions based on the assumption that R equals the Bjerrum parameter q , Eq.

Table II. Comparison of the Results at 25 °C with Literature Data*

Salt	Original data	Redetermination with the method of this paper: $R = a + s$, or $a' + s$					
		First author's name Year, Literature, Method**	Λ_0	K_A	Λ_0	K_A	σ_{fit}
LiCl(a')	Shkodin 1968 [11] a,b,c	23.1	1000	24.8 ± 0.3	1110 ± 110	0.3	7-48
	Evans 1971 [26] e	20.09	210				
	This paper			20.017±0.007	297 ± 1	0.004	14-50
NaI(a')	Gover 1956 [13] b	23.92	189	23.93±0.04	197 ± 10	0.03	8-36
	Wikander 1972 [14] d	24.338	122.8	24.39±0.01	202 ± 2	0.01	10-46
	This paper			24.297±0.005	205.3±0.9	0.004	11-45
KI	Hovorka 1937 [12] c	25.16	244	25.22±0.04	281 ± 12	0.03	9-32
	Gover 1956 [13] b	25.75	333	25.75±0.03	321 ± 12	0.02	7-27
	Wikander 1972 [14] d	26.302	279.9	26.35±0.01	344 ± 2	0.01	11-46
	This paper			26.07±0.02	336 ± 5	0.01	12-33
KSCN	Gover 1956 [13] b	26.12	323	26.17±0.02	320 ± 5	0.01	9-32
	This paper			26.593±0.002	330.1±0.2	0.0008	17-54
RbI	Wikander 1972 [14] d	26.959	430.6	26.99±0.01	472 ± 3	0.01	9-32
	This paper			26.57±0.02	433 ± 7	0.02	8-32
Et ₄ NI	Gover 1956 [13] b	28.55	588	28.52±0.02	564 ± 6	0.01	8-25
	Evans 1968 [15] e	29.01	466	29.15±0.02	564 ± 2	0.005	15-43
	This paper			28.985±0.008	543 ± 3	0.007	7-23
Pr ₄ NI	Gover 1956 [13] b	24.50	385	25.82±0.03	504 ± 10	0.02	7-30
	Evans 1968 [15] e	26.08	391	26.339±0.004	523.3±0.6	0.001	19-47
	This paper			26.277±0.006	515 ± 1	0.005	8-42
Bu ₄ NI	Evans 1968 [15] e	24.60	415	24.782±0.004	541.9±0.6	0.001	18-44
	DeLisi 1973 [16] f	24.56	412	24.65±0.02	529 ± 4	0.002	19-32
	This paper			24.66±0.02	517 ± 8	0.02	6-31
Bu ₄ NC10 ₄	Evans 1968 [15] e	27.13	769	27.34±0.02	912 ± 3	0.005	16-43
	This paper			27.186±0.005	904 ± 1	0.004	8-40
Bu i-Am ₃ NI	Evans 1968 [15] e	24.02	462	24.123±0.005	576 ± 1	0.002	14-41
	This paper			24.111±0.005	568 ± 1	0.004	9-44

*Units: molar conductance Λ , S-cm²-mol⁻¹; association constant K_A , mol⁻¹-dm³; standard deviation σ_{fit} , S-cm²-mol⁻¹. **Method of data analysis in the original paper: a, Kraus-Bray (J. Am. Chem. Soc. 35 (1913) 1315); b, Fuoss-Shedlovsky (J. Am. Chem. Soc. 71 (1949) 1496); c, Fuoss-Kraus (J. Am. Chem. Soc. 55 (1933) 476); d, Fuoss-Onsager (J. Phys. Chem. 61 (1957) 668); e, Fuoss-Onsager (R. M. Fuoss and F. Accascina, Electrolyte Conductance, Intersc., New York 1959); f, Fuoss-Onsager-Skinner (J. Phys. Chem. 69 (1965) 2581).

(2a), is reported in Ref. 10. These studies led us to adopt the standard procedure used in this and preceding papers, see Ref. 1.

The conductance data for 1-propanol solutions at 25 °C from the literature and from this paper are compared in Table II. For this purpose, limiting conductances Λ_0 and association constants K_A of the literature were redetermined with the help of CM calculations as outlined in this paper for the original conductance data which permitted

Table III. Limiting Conductances of Salts in 1-Propanol from
-40 to 25 °C ^a

Salt	25 °C	10 °C	0 °C	-10 °C	-20 °C	-30 °C	-40 °C
LiCl(a')	20.01 ₇	13.59 ₆	10.29 ₉	7.66 ₆	5.59 ₁	3.98 ₄	2.76 ₀
NaBr(a')	22.65 ₃	15.47 ₀	11.76 ₄	8.78 ₉	6.43 ₆	4.60 ₃	3.19 ₇
NaI(a')	24.29 ₇	16.67 ₂	12.72 ₆	9.54 ₆	7.01 ₅	5.04 ₀	3.51 ₅
KI	26.0 ₇	17.8 ₈	13.6 ₄	10.21 ₆	7.49 ₇	5.37 ₄	3.73 ₉
KSCN	26.59 ₃	18.26 ₆	13.94 ₃	10.45 ₁	7.66 ₈	5.49 ₆	3.82 ₃
RbI	26.5 ₇	18.2 ₈	13.9 ₇	10.4 ₈	7.70 ₈	5.53 ₅	3.85 ₈
Et ₄ NI	28.98 ₅	20.00 ₇	15.32 ₀	11.51 ₆	8.48 ₃	6.08 ₁	4.25 ₉
Pr ₄ NI	26.27 ₇	18.07 ₃	13.80 ₂	10.34 ₈	7.60 ₀	5.44 ₈	3.79 ₀
Bu ₄ NI	24.6 ₆	16.9 ₆	12.9 ₆	9.71 ₄	7.13 ₄	5.11 ₆	3.56 ₁
Bu ₄ NClO ₄	27.18 ₆	18.87 ₀	14.50 ₉	10.95 ₉	8.11 ₁	5.86 ₄	4.11 ₅
<i>n</i> -Am ₄ NI	23.53 ₁	16.19 ₄	12.37 ₈	9.29 ₃	6.83 ₄	4.90 ₈	3.42 ₁
<i>i</i> -Am ₄ NI	23.78 ₈	16.35 ₅	12.49 ₂	9.36 ₈	6.88 ₄	4.93 ₈	3.43 ₉
Hept ₄ NI	21.9 ₉	15.1 ₄	11.5 ₇	8.67 ₉	6.37 ₇	4.57 ₂	3.17 ₃
MeBu ₃ NI	25.45 ₅	17.51 ₁	13.37 ₂	10.03 ₄	7.37 ₃	5.29 ₁	3.68 ₆
Me ₂ Bu ₂ NI	26.56 ₂	18.27 ₆	13.96 ₉	10.47 ₉	7.70 ₄	5.52 ₇	3.84 ₈
EtBu ₃ NI	25.54 ₀	17.56 ₄	13.41 ₃	10.04 ₉	7.37 ₄	5.28 ₁	3.66 ₂
<i>i</i> -Am ₃ BuNI	24.11 ₁	16.57 ₃	12.65 ₄	9.48 ₇	6.96 ₉	4.99 ₈	3.47 ₆
<i>i</i> -Am ₃ BuN- BPh ₄	21.0 ₅	14.5 ₁	11.0 ₉	8.3 ₁	6.0 ₇	4.32 ₄	2.97 ₃

^aUnits: Λ_{∞} , S-cm²-mol⁻¹.

the use of our programs. The dimensionless quantity κq characterizes the concentration range of the measurements. It is interesting to state that these re-evaluations generally entail better values of σ_{fit} than the original procedures. Comparison is limited by unknown experimental factors, such as purity of the products and protection of the iodides from light, protection of the solutions by an inert gas, and details of the measuring techniques.

Precise determinations of association constants at 25 °C based on the chemical model are known from calorimetric measurements of heats of dilution⁽¹⁷⁾ (K_A , mol⁻¹-dm³): 314 (NaBr), 206 (NaI), 374 (KI), 527 (RbI), 535 (Et₄NI), 513 (Pr₄NI), 534 (Bu₄NI), 536 (*n*-Am₄NI), 581 (*i*-Am₄NI), 597 (MeBu₃NI), 691 (Me₂Bu₂NI), 535 (EtBu₃NI), and 559 (*i*-Am₃BuNI). The results of these measurements are compared to our conductance data in Section 3.2. Suffice it to say here that the agreement of the association constants at 25 °C from calorimetric and conductance measurements, Tables II and V, is satisfactory.

Table IV. Limiting Ionic Conductances for 1-Propanol Solutions at 25 and 10 °C ^a

Ion	Transf. Numbers KSCN	25 °C, based on		10 °C, based on	
		Walden Values	Transf. Numbers NaBr, NaI	Transf. Numbers KSCN	Walden Values
Na ⁺	10.60	10.50 ^e	10.34 ^f	7.16	7.19 ^e
K ⁺	12.37 ^b	12.27 ^e		8.37 ^b	8.40 ^e
Rb ⁺	12.87			8.77	
Et ₄ N ⁺	15.29			10.50	
Pr ₄ N ⁺	12.58			8.56	
Bu ₄ N ⁺	10.97	10.83 ^c		7.45	7.50 ^c
<i>m</i> -Am ₄ N ⁺	9.83	9.69 ^c		6.68	6.71 ^c
<i>i</i> -Am ₄ N ⁺	10.09	10.01 ^c		6.85	6.82 ^c
<i>n</i> -Hept ₄ N ⁺	8.29	8.24 ^c		5.63	5.70 ^c
MeBu ₃ N ⁺	11.76			8.00	
Me ₂ Bu ₂ N ⁺	12.86			8.77	
EtBu ₃ N ⁺	11.84			8.05	
<i>i</i> -Am ₃ BuN ⁺	10.41			7.06	
Br ⁻	12.05		12.31	8.31	
I ⁻	13.70	13.80 ^d	13.96	9.51	9.48 ^d
SCN ⁻	14.22			9.90	
ClO ₄ ⁻	16.22			11.42	
BPh ₄ ⁻	10.64			7.45	

^aUnits: limiting conductances λ_o , S-cm²-mol⁻¹. ^bReference value from transference number measurements.⁽²⁾ ^cCalculated from $\lambda_o\eta_s = 0.2131$ (Bu₄N⁺), 0.1906 (*n*-Am₄N⁺), 0.1936 (*i*-Am₄N⁺), 0.1620 (*n*-Hept₄N⁺) from Ref. 19 and viscosities at 25 and 10 °C (Table I). ^dMean values for (I⁻) from Walden values and limiting conductances (Table III). ^eBased on mean value for λ (I⁻). ^fReference value from transference number measurements (mean value for Na⁺ from NaBr and NaI), Refs. 20 and 21.

3.1. Limiting Conductances

Table III shows the limiting conductance results from the data analysis described above. Alternative evaluations of Λ_o for lithium and sodium salts based on the assumption $R = a + s$ (instead of $R = a' + s$, Table III) didn't show significant difference, as expected from our studies on ethanol solutions.⁽¹⁾

Transference numbers of KSCN in 1-propanol are known at 25 and 10 °C:⁽²⁾ t_o^+ (25 °C) = 0.4654 ± 0.0005 and t_o^+ (10 °C) = 0.4583

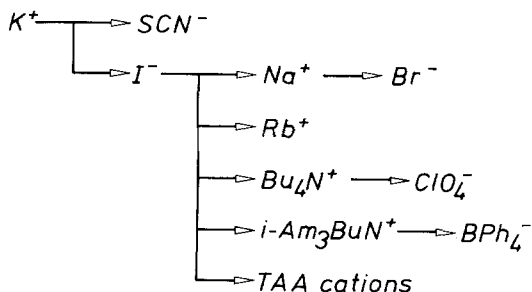


Fig. 1. Flow diagram for the calculation of the limiting ionic conductances from transference numbers of KSCN in 1-propanol at 25 and 10 °C given in Table IV.

± 0.0015 . They were used for the calculation of limiting conductances in Table IV, columns 1 and 4, following the scheme of Fig. 1.

Columns 2 and 5, Table IV, show single ion conductances which were independently determined from Walden values. This method is known to produce reasonably well approximated data for voluminous organic ions in various nonaqueous solvents;⁽¹⁸⁾ the reference data for Bu_4N^+ , $n\text{-Am}_4\text{N}^+$, $i\text{-Am}_4\text{N}^+$, and $n\text{-Hept}_4\text{N}^+$ were used to calculate the mean value of $\lambda_o(\text{I}^-)$ with the help of the limiting conductances of the corresponding tetraalkylammonium iodide conductances of Table III. Similar methods were used by Evans and Gardam ($i\text{-Am}_3\text{BuN}^+$ and $n\text{-Hex}_4\text{N}^+$)⁽¹⁵⁾ and De Lisi and Goffredi (Bu_4N^+),⁽¹⁶⁾ their values are in reasonable agreement with Table IV. Gill⁽²²⁾ used the equipartition of $\Lambda_o(\text{Bu}_4\text{NBBu}_4)$ into equal parts for anion and cation to yield $\lambda_o(\text{Bu}_4\text{N}^+) = 10.51 \text{ S}\cdot\text{cm}^2\cdot\text{mol}^{-1}$ [from $\Lambda_o = (21.01 \pm 0.10)$ after re-evaluation of Gill's data according to the CM]. The limiting conductances of Marx *et al.*^(20,21) are quoted in Table IV, column 3. They are based on transference numbers of NaI and NaBr in 1-propanol solutions using Co^{2+} as boundary indicator. Wikander and Isacson⁽¹⁴⁾ used the transference numbers of alkali metal ions in ethanol also for 1-propanol solutions claiming a precision of about 2%. This claim is justified by our determination of the cation transference numbers of KSCN in ethanol and 1-propanol by a moving boundary method,⁽²⁾ $t_o(\text{K}^+, \text{EtOH}) = 0.4590 \pm 0.0003$ and $t_o(\text{K}^+, \text{PrOH}) = 0.4654 \pm 0.0005$.

Comparison of $\lambda_o[i\text{-Am}_3\text{BuN}^+]$ and $\lambda_o[\text{BPh}_4^-]$ indicates that splitting of $\Lambda_o[i\text{-Am}_3\text{BuNBPh}_4]$ into equal contributions for cation and anion in 1-propanol solutions (2% difference at 25 °C, 6% at 10 °C) is more favorable than in ethanol solutions (7% at 25 °C, 8% at -5 °C).⁽¹⁾

Taking into account the possible uncertainties and sources of error, our data at 25 °C (column 1) and 10 °C (column 4) show a preci-

sion of about 1% or better.

The slopes at 25 °C, $d(\ln \lambda_o)/d(1/T)$, for all cations are found to be $(-2.17 \pm 0.05) \times 10^3$, and for all anions within $(-2.05 \pm 0.04) \times 10^3$, viscosity data of pure 1-propanol yield $-d(\ln \eta_s)/d(1/T) = -2.1 \times 10^3$, again indicating that the activation energies of ionic transport do not vary significantly for ions of different size, *cf.* Ref. 1, and are comparable to the activation energy of viscous flow of the solvent, *cf.* Ref. 8.

Positive slopes of the Walden products, $d(\ln \eta_s \lambda_o)/dT$, are found for the cations, negative or zero slopes for the anions which might be interpreted in terms of structure promoting or breaking ionic effects.⁽²³⁻²⁵⁾

3.2. Association Constants

The association constants K_A for all salts are quoted in Table

Table V. Association Constants for Salts in 1-Propanol in the Temperature Range -45 to 25 °C^a

Salt	25 °C	10 °C	0 °C	-10 °C	-20 °C	-30 °C	-40 °C
LiCl(a')	2.9 ₇	2.0 ₀	1.58 ₉	1.29 ₄	1.07 ₃	0.90 ₉	0.79 ₃
NaBr(a')	3.08	2.13	1.71 ₀	1.42 ₄	1.21 ₀	1.05 ₀	0.94 ₀
NaI(a')	2.05 ₃	1.50 ₆	1.26 ₅	1.08 ₇	0.94 ₃	0.85 ₁	0.76 ₈
KI(a)	3.3 ₆	2.3 ₅	1.9 ₀	1.5 ₆	1.2 ₉	1.0 ₉	0.9 ₁
KSCN(a)	3.301	2.373	1.949	1.627	1.365	1.164	1.000
RbI(a)	4.3 ₃	3.1 ₁	2.5 ₄	2.1 ₀	1.7 ₅	1.4 ₈	1.2 ₄
Et ₄ NI	5.4 ₃	4.9 ₂	4.7 ₂	4.5 ₈	4.5 ₈	4.7	4.7 ₈
Pr ₄ NI	5.1 ₅	4.73 ₀	4.58 ₈	4.53 ₅	4.5 ₇	4.6 ₇	4.8 ₆
Bu ₄ NI	5.1 ₇	4.7 ₇	4.6 ₄	4.5 ₅	4.5 ₈	4.6 ₇	4.8 ₃
Bu ₄ NClO ₄	9.0 ₄	8.8 ₉	9.0 ₂	9.3 ₃	9.8 ₅	10.6 ₂	11.6 ₄
<i>n</i> -Am ₄ NI	5.3 ₇	4.9 ₉	4.87 ₆	4.85 ₂	4.89 ₈	5.0 ₁	5.2 ₃
<i>i</i> -Am ₄ NI	5.7 ₃	5.3 ₅	5.2 ₃	5.2 ₁	5.2 ₇	5.4 ₂	5.6 ₇
Hept ₄ NI	5.0 ₉	4.6 ₅	4.4 ₆	4.3 ₆	4.2 ₈	4.2 ₃	4.1 ₄
MeBu ₃ NI	6.0 ₇	5.5 ₆	5.3 ₆	5.29 ₆	5.3 ₁	5.4 ₄	5.69 ₀
Me ₂ Bu ₂ NI	6.6 ₅	6.0 ₁	5.7 ₉	5.6 ₇	5.6 ₆	5.7 ₆	5.9 ₆
EtBu ₃ NI	5.41 ₃	4.95 ₄	4.7 ₉	4.7 ₀	4.6 ₆	4.7 ₂	4.8 ₀
<i>i</i> -Am ₃ BuNI	5.6 ₈	5.2 ₈	5.1 ₅	5.1 ₂	5.1 ₆	5.2 ₉	5.5 ₀
<i>i</i> -Am ₃ BuN	6.1	7.0	7.8	8.9	10.1	11.5	13.4
BPh ₄							

^a All constants are given as values of $K_A \times 10^{-2}$. Units: K_A , mol⁻¹·dm³.

V. CM calculations suggest the interpretation of association constants by the help of the relationship (cgs units).^(1,3)

$$K_A = 4\pi N_A \times 10^{-3} \exp\left[-\frac{\Delta G^*}{RT}\right] \int_{a \text{ or } a'}^R r^2 \exp\left[-\frac{2q}{r}\right] dr \quad (4)$$

where $\Delta G^* = N_A W_{+-}^*$; W_{+-}^* is that part of the potential of the mean forces between cations and anions which is due to the non-coulombic interactions⁽³⁾

$$W_{+-}^* = \text{constant, if } a \text{ or } a' \leq r \leq R$$

$$W_{+-}^* = 0, \quad \text{if } r \geq R$$

The other symbols of Eq. (4) have their usual meaning.

In Eq. (4), a' is the distance of closest approach between cation and anion in the solution given by the configuration $[C^+(\text{OH})A^-]$ for lithium and sodium salts and a is the cation-anion distance of the contact pair $[C^+A^-]$ used for all other salts, R is given by the configurations $[C^+(\text{OH})(\text{C}_3\text{H}_7\text{OH})A^-]$ and $[C^+(\text{C}_3\text{H}_7\text{OH})A^-]$, respectively.

Alkali metal and tetraalkylammonium salts exhibit quite different K_A behavior as shown in Figs. 2 and 3, in complete agreement with the results on ethanol solutions.⁽¹⁾ Alkali metal salts show association constants which increase at increasing temperatures, whereas those for tetraalkylammonium salts show shallow minima, except *i*-Am₃BuNBPh₄ which shows a negative temperature coefficient, $dK_A/dT < 0$. The temperature at which the minimum is attained is almost equal for the tetraalkylammonium iodides (except Hept₄NI); it is significantly shifted to higher values with increasing anion size for Bu₄NClO₄ and *i*-Am₃BuNBPh₄. These results are independent of the choice of R within reasonable limits.

As was the case for ethanol solutions, the different behavior of alkali metal and tetraalkylammonium salts can be understood from the role of the non-coulombic contributions in ion-pair formation. The Gibbs' energy of ion-pair formation

$$\Delta G_T^\circ = -RT \ln K_A \quad (5)$$

can be split into two parts

$$\Delta G_T^\circ = \Delta G^{\text{coul}} + \Delta G^* \quad (6)$$

according to Eq. (4). The molarity scale is used throughout for the fol-

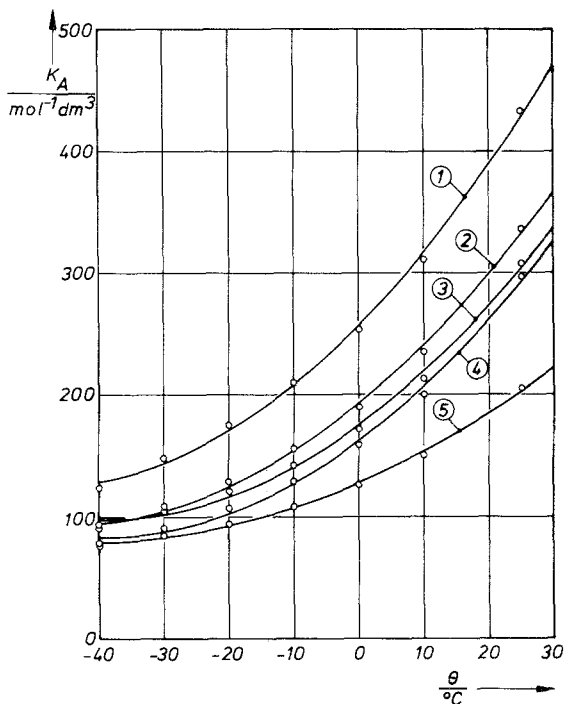


Fig. 2. Temperature dependence of the association constants of alkali metal salts in 1-propanol solutions; RbI (1), KI (2), NaBr (3), LiCl (4), and NaI (5).

lowing calculations; conversion into the molality scale can be done easily,⁽¹⁾ but doesn't change the features of our discussion.

Table VI compiles the coefficients A_0 , A_1 , and A_2 of the following polynomials calculated from the temperature dependence of K_A

$$\Delta G_T^\circ = A_0 + A_1(298.15 - T) + A_2(298.15 - T)^2 \quad (7a)$$

$$\Delta S_T^\circ = A_1 + 2A_2(298.15 - T) \quad (7b)$$

$$\Delta H_T^\circ = A_0 + 298.15 A_1 + A_2[(298.15)^2 - T^2] \quad (7c)$$

ΔH_T° and ΔS_T° are the enthalpy and entropy of ion-pair formation.

The values of ΔG_{298}° , ΔH_{298}° , and ΔS_{298}° at 25 °C then are

$$\Delta G_{298}^\circ = A_0; \quad \Delta S_{298}^\circ = A_1; \quad \Delta H_{298}^\circ = A_0 + 298.15 A_1 \quad (8a, b, \text{ and } c)$$

As usual, the values of ΔG_{298}° provide no useful information on ion-pair

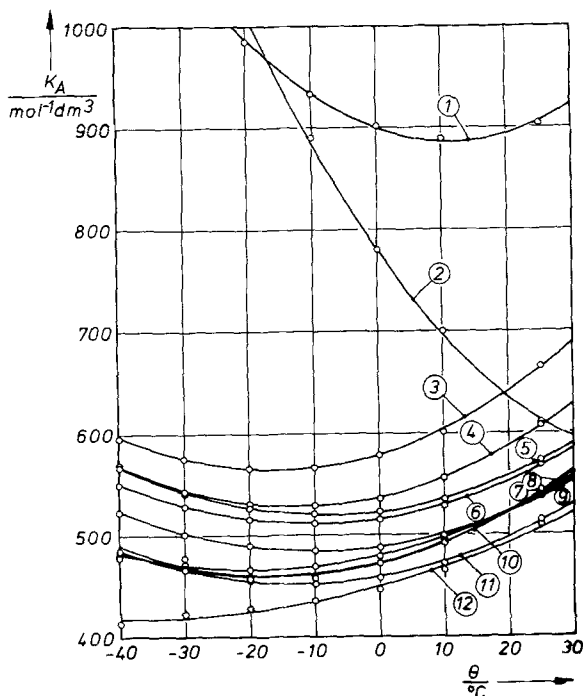


Fig. 3. Temperature dependence of the association constants of tetraalkylammonium salts in 1-propanol solutions: Bu_4NClO_4 (1), $i\text{-Am}_3\text{BuNBPh}_4$ (2), $\text{Me}_2\text{Bu}_2\text{NI}$ (3), MeBu_3NI (4), $i\text{-Am}_4\text{NI}$ (5), $i\text{-Am}_3\text{BuNI}$ (6), Et_4NI (7), Pr_4NI (8), EtBu_3NI (9), $n\text{-Am}_4\text{NI}$ (10), Bu_4NI (11), and Hept_4NI (12).

formation. They lie between -13 and $-17 \text{ kJ}\cdot\text{mol}^{-1}$ for both alkali metal and tetraalkylammonium salts. The values of ΔS_{298}° and ΔH_{298}° , however, exhibit a significant pattern. Alkali metal salts show entropy values around their mean value of $106 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$, tetraalkylammonium salts around $67 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$, with the exception of $i\text{-Am}_3\text{BuNBPh}_4$. The ΔH_{298}° values of alkali metal salts are all about $17.5 \text{ kJ}\cdot\text{mol}^{-1}$. Tetraalkylammonium salts show enthalpies less than 5; the shift of the minima, Fig. 3, to higher temperatures in the sequence $\text{I}^- < \text{ClO}_4^- < \text{BPh}_4^-$ is reflected in Table VI by decreasing enthalpies. It might be interesting (although of minor importance) to mention that the tetraalkylammonium iodides of the type $\text{R}_n\text{R}'_{4-n}\text{NI}$ exhibit an empirical rule given by the relationship

$$\Delta H_{298}^\circ(\text{R}_n\text{R}'_{4-n}\text{NI}) = 1/4[n\Delta H_{298}^\circ(\text{R}_4\text{NI}) + (4-n)\Delta H_{298}^\circ(\text{R}'_4\text{NI})] \quad (9)$$

e.g., for $i\text{-Am}_3\text{BuNI}$ the observed (Table VI) and estimated [Eq. (9)]

Table VI. Coefficients of Polynomials in Eq. (7a) for Various Salts in 1-Propanol ^{a,b}

Salt	A_0^c	A_1^d	A_2	σ_{fit}	$A_0 + 298.15A_1^e$
LiCl(a')	-14102.4	113.923	-0.422597	10.3	19863.7
NaBr(a')	-14195.2	110.831	-0.431488	10.8	18849.1
NaI(a')	-13188.3	96.5670	-0.359159	16.6	15603.2
KI	-14409.9	107.215	-0.313094	16.8	17556.3
KSCN	-14367.1	102.809	-0.296483	12.8	16285.4
RbI	-15038.2	105.031	-0.271307	15.0	16276.8
Et ₄ NI	-15599.4	70.0512	-0.223141	30.5	5286.4
Pr ₄ NI	-15472.7	67.2109	-0.212260	11.3	4566.2
Bu ₄ NI	-15480.7	66.4499	-0.195453	9.7	4331.3
Bu ₄ NClO ₄	-16867.2	61.0904	-0.188731	9.7	1346.9
<i>n</i> -Am ₄ NI	-15574.2	65.2114	-0.190927	10.5	3868.6
<i>i</i> -Am ₄ NI	-15736.1	65.3807	-0.191760	9.5	3757.2
<i>n</i> -Hept ₄ NI	-15434.6	65.5441	-0.124236	21.4	4107.4
MeBu ₃ NI	-15881.2	69.7741	-0.226655	8.7	4921.9
Me ₂ Bu ₂ NI	-16101.0	71.7304	-0.226477	12.1	5285.4
EtBu ₃ NI	-15593.1	67.4863	-0.183177	12.8	4527.9
<i>i</i> -Am ₃ BuNI	-15713.5	65.7599	-0.189400	10.8	3892.8
<i>i</i> -Am ₃ BuNBPh ₄	-15896.7	30.6883	-0.152435	15.0	-6747.0

^a Units: ΔG_T^0 , J-mol⁻¹. ^b The numerical results in this table are not limited to significant numbers, thus permitting the reproduction of measurements with the original precision. ^c $A_0 = \Delta G_{298}^0$, J-mol⁻¹. ^d $A_1 = \Delta S_{298}^0$, J-mol⁻¹-K⁻¹. ^e $A_0 + 298.15 A_1 = \Delta H_{298}^0$, J-mol⁻¹.

ΔH_{298}^0 values are 3.9 and 4.0, respectively; the enthalpy of ion-pair formation for Et₄NI is estimated to be 5.2 from EtBu₃NI in comparison to 5.3, Table VI.

The difference between the mean value of the tetraalkylammonium salts and *i*-Am₃BuNBPh₄ in ΔS_{298}^0 is 35 J-mol⁻¹-K⁻¹, and in ΔH_{298}^0 is 11 kJ-mol⁻¹. This is exactly the same pattern which was observed for ethanol solutions. Again, the difference in ΔH_{298}^0 and ΔS_{298}^0 for alkali metal and tetraalkylammonium salts, and the almost equal decrease with regard to the other tetraalkylammonium salts produced by the tetraphenylborate ion, indicate that replacing a solvated cation or anion by an unsolvated species entails about the same effect on the non-coulombic parts of the mean force potentials.

For ethanol solutions, we published the scales of ΔH^* (kJ-mol⁻¹) and ΔS^* (J-mol⁻¹-K⁻¹) values.⁽¹⁾ The corresponding scales for 1-

propanol solutions also exhibit LiCl at the highest ($\Delta S_{298}^* = 47$, $\Delta H_{298}^* = 11.6$) and *i*-Am₃BuNBPh₄ at the lowest ($\Delta S_{298}^* = -21$, $\Delta H_{298}^* = -11.7$) places. The other tetraalkylammonium salts show small values of ΔS_{298}^* around 6 and negative enthalpies, $\Delta H_{298}^* < -2$. The alkali metal salts exhibit distinctly larger entropies, $\Delta S_{298}^* > 20$, and positive enthalpies, $\Delta H_{298}^* > 4$. Hence, the main features of association are equal both in ethanol and 1-propanol and do not need repeated discussion for 1-propanol solutions.

Heat of dilution measurements at 25 °C yield K_A and ΔH_{298}^0 by CM calculations⁽¹⁷⁾ and hence also ΔS_{298}^0 . Table VII compares the results from such calorimetric measurements and the conductance data of this paper.

Table VII. Comparison of Enthalpies and Entropies of Ion-Pair Formation from Heat of Dilution (Ref. 17) and Conductance (this Paper)^a

Electrolyte	Heat of Dilution ^{b,c}			Conductance		
	<i>R</i>	ΔH_{298}^0	ΔS_{298}^0	<i>R</i>	ΔH_{298}^0	ΔS_{298}^0
NaBr				12.7	18.8	111
	9.2	22.1	122	(9.2)	(20.3)	(115)
NaI				12.9	15.6	97
	9.7	18.9	107	(9.7)	(17.2)	(101)
KI				10.4	17.6	107
	9.9	19.1	113	(9.9)	(18.1)	(109)
RbI				10.6	16.2	105
	9.5	17.5	111	(9.5)	(16.5)	(106)
Et ₄ NI	13.1	6.6	75	13.1	5.3	70
Pr ₄ NI	13.6	6.0	72	13.6	4.6	67
Bu ₄ NI	14.0	5.7	71	14.0	4.3	66
<i>n</i> -Am ₄ NI	14.4	5.6	71	14.4	3.9	65
<i>i</i> -Am ₄ NI	14.1	5.2	70	14.1	3.8	65
MeBu ₃ NI	12.6	6.4	75	12.6	4.9	70
Me ₂ Bu ₂ NI	12.6	7.0	78	12.6	5.3	72
EtBu ₃ NI	13.1	5.9	72	13.1	4.5	68
<i>i</i> -Am ₃ BuNI	14.1	5.3	71	14.1	3.9	66

^a Units: *R*, Å; ΔH_{298}^0 , kJ·mol⁻¹; ΔS_{298}^0 , J·mol⁻¹·K⁻¹. ^b Distance parameters *R* for alkali metal salts from least squares fits of calorimetric measurements; *R* for tetraalkylammonium salts is $\alpha + s$ (cf. conductance measurements). ^c Data analysis of tetraalkylammonium salts includes an empirical $m^{3/2}$ term which is not given by the chemical model.

The agreement of the association constants K_A from both methods was shown in Chapter 3. Both methods also yield comparable values of ΔH_{298}° and ΔS_{298}° . In Table VII, columns 2(R), 3(ΔH_A°), and 4(ΔS_A°) show the results from calorimetric,⁽¹⁷⁾ and columns 5(R), 6(ΔH_{298}°), and 7(ΔS_{298}°) show those from conductance (this paper) measurements.

With regard to the chemical model, the differences in the data analysis of calorimetric and conductance results are of minor importance, except the use of R values from least squares fits of alkali metal salts. These R values are systematically smaller than the estimated values used for conductance measurements; a re-evaluation of the conductance measurements (data in parentheses) exhibits the influence of R . The differences in absolute values are caused by the simple fact that the determination of ΔH_{298}° and ΔS_{298}° from conductance data requires the tangent at the curve ΔG_T° vs. T which is ill-defined at 25 °C. The temperature of 25 °C is the highest temperature used in the conductance series (values of K_A and hence ΔG_{298}° from conductance and calorimetric measurements are in good agreement) but the polynomial, Eq. (7a), doesn't reproduce the tangent at 25 °C (end of the interval) with a sufficiently steep slope; tentative evaluations with polynomials of fourth degree yield good agreement also for the ΔH_{298}° and ΔS_{298}° values from both methods.

To sum up the results of this comparison, the patterns of ΔH_{298}° and ΔS_{298}° from conductance and calorimetric measurements are the same; arranged in increasing enthalpies or entropies yields the same sequence of salts in both series with the same significant step for ΔH_{298}° and ΔS_{298}° between alkali metal and tetraalkylammonium salts. Taking into account that the equality of the association constants (K_A or ΔG_{298}°) and their temperature coefficients (ΔS_{298}°) is a highly pretentious criterion for the reliability of the model, the agreement in Table VII is satisfactory.

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