

pared to the corresponding mixture of an m_c -membered cyclic monoether with the same n -alkane and (b) $\partial V^E/\partial T$ increases with increasing chain length of the n -alkane for the series with six-membered cyclic ethers, whereas for the series containing five-membered cyclic ethers $\partial V^E/\partial T$ decreases slightly with increasing n .

A detailed discussion of all our results on mixtures of cycloethers with n -alkanes, including data reported in ref 19, is deferred until heat capacities and ultrasonic speeds are available.

Registry No. Oxolane, 109-99-9; oxane, 142-68-7; 1,3-dioxolane, 646-06-0; 1,4-dioxane, 123-91-1; n -heptane, 142-82-5; n -decane, 124-18-5; n -tetradecane, 629-59-4.

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Received for review February 23, 1982. Accepted August 16, 1982.

Electrical Conductivity of Concentrated Lithium Bromide Aqueous Solutions

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The electrical conductivity of aqueous lithium bromide solutions was measured at the concentrations of 40-63 wt % of LiBr (6.5-13 M) and temperatures of 15-80 °C. The results are reproducible to within $\pm 0.4-1.5\%$ (3 mmho) and are suitable for analytical determination of LiBr. The absolute accuracy of analytical determination using this method is $\pm 0.3\%$ LiBr in concentrations greater than 50% and $\pm 0.7\%$ in concentrations of 40-50% LiBr. Data compare favorably with previous publications.

Concentrated lithium bromide solutions are used in absorption air conditioning machines. These are used as central units to

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control the temperature and humidity in buildings where there is waste steam, or in places where the vibrations created by centrifugal central air conditioners are unacceptable (1, 2). Absorption air conditioners are also important in solar energy utilization (3). Thus, the determination of LiBr in concentrated solution is of practical value.

There are two known methods for the determination of LiBr: by titration with AgNO_3 (4) and by measurement of the density of the solution (5). Both methods give accurate results and correspond to each other (6). However, another analytical method may be derived, one that does not require expensive reagents, skilled technical personnel, or large volumes of sample. Such a method could be measurement of conductivity of the LiBr solution. Moreover, conductivity values could be measured inside the machine, without having to extract samples.

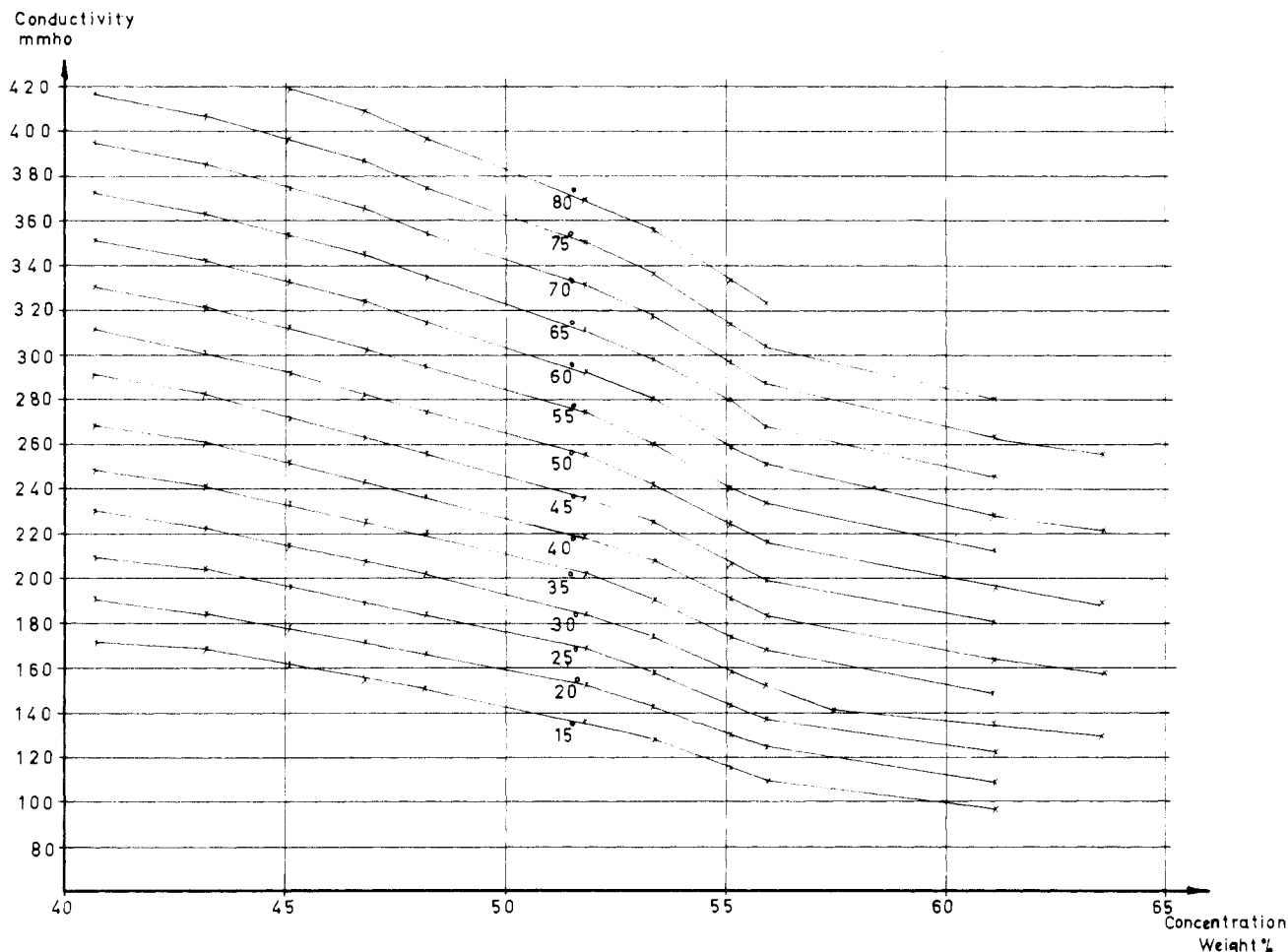


Figure 1. Specific conductance of LiBr solutions as a function of concentration at various temperatures. Concentration is given in weight percent of LiBr.

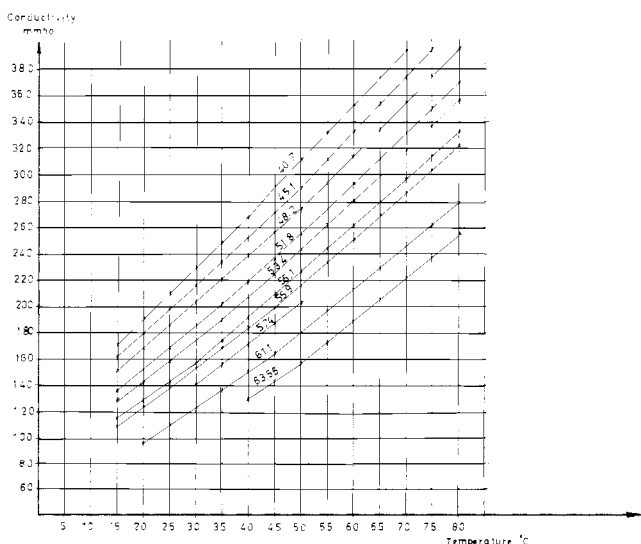


Figure 2. Specific conductance of LiBr solutions as a function of temperature at various concentrations.

The measurement of conductivity in concentrated solution is generally considered inadequate for analytical purposes since the change of the function (conductivity) with concentration is very small and unpredictable. However, by using a conductometer which uses square wave for measurement with a sampling technique (7), we obtained very reproducible results.

Experimental Section

Solutions were prepared by using anhydrous LiBr supplied by the Lithium Corporation of America. The concentration was determined as weight percent by titration with AgNO_3 using eosin or $\text{Na}_2\text{Cr}_2\text{O}_7$ for end-point detection, and by measuring the density of the solution at a thermostated 25 °C.

Conductivity was measured in a temperature-controlled bath at temperatures fixed to within ± 0.1 °C. The procedure was to heat the solution to the lowest temperature, equilibrate it, measure the conductivity, and go on to the next temperature. When the maximum temperature was reached, the procedure was repeated when cooling the solution.

The solutions were kept all the time in glass-stoppered flasks, even while measuring the conductance.

The results from several measurements were reproducible within 3 mmho (± 1.5 mmho).

The results of these measurements were used in the analysis of LiBr solutions taken out of absorption machines. The results were checked by titration or by density measurements and were accurate to $\pm 0.2\%$.

Results and Discussion

The conductivity of concentrated LiBr solutions was studied by Baron et al. (8) and Molenat (9). Their data give values for a range of concentrations (42–53 wt %) for 25 °C (9) and for two concentrations (42 and 49.8 wt %) at a range of temperatures (15–70 °C) (8). These data are too limited to use

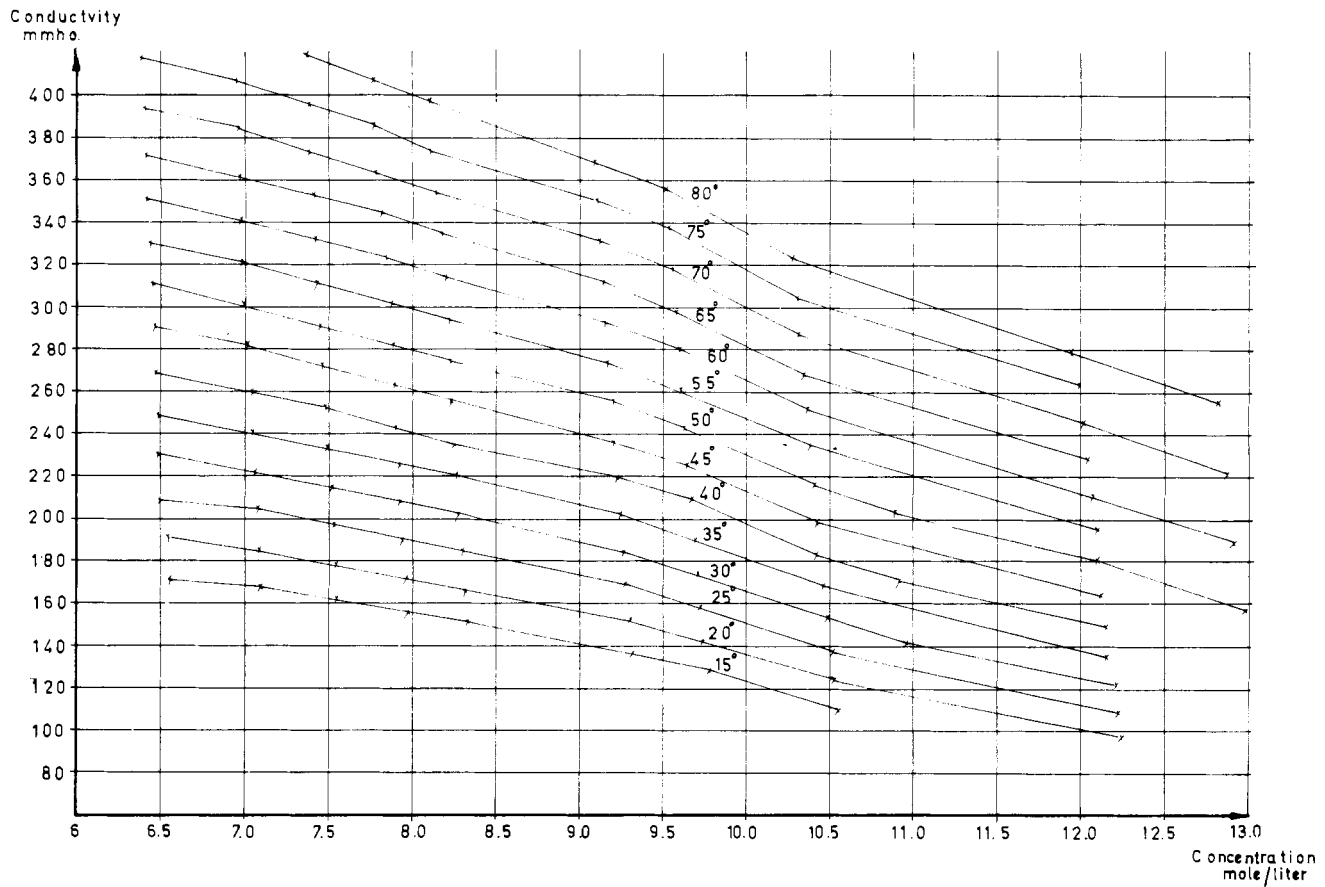


Figure 3. Specific conductance of LiBr solutions as a function of concentration at various temperatures. Concentration is given in mol of LiBr/(L of solution).

Table I. Specific Conductance (mmho) of LiBr Solutions

[LiBr], wt %	temp, °C	15	20	25	30	35	40	45	50	55	60	65	70	75	80
40.7		171	191	209	230	248	268	291	311	330	351	372	394	417	442
43.2		168	185	204	222	241	260	282	301	321	342	363	385	407	430
45.1		162	179	197	215	233	252	271	292	312	333	354	374	396	419
46.7		155	171	189	207	225	243	263	282	302	324	345	365	387	409
48.2		151	166	184	202	220	236	255	274	294	314	334	354	374	396
51.8		136	152	169	184	202	219	236	255	274	292	311	331	350	369
53.35		128	142	158	174	190	208	225	242	260	280	298	318	337	356
55.1		115	129	143	158	174	190	206	224	240	259	280	298	314	333
55.9		109	124	137	153	168	183	199	216	234	251	268	287	304	323
57.4					141	170	179								
61.1			97	109	122	135	149	164	180	195	212	228	245	263	280
63.55						129	129		157		189	228	221	263	255

Table II. Density (g/mL) of LiBr Solutions

[LiBr], wt %	temp, °C	15	20	25	30	35	40	45	50	55	60	65	70	75	80
40.7		1.396	1.393	1.390	1.388	1.385	1.383	1.380	1.377	1.375	1.372	1.370	1.367	1.365	1.362
43.2		1.429	1.427	1.424	1.421	1.418	1.416	1.413	1.410	1.407	1.405	1.402	1.400	1.397	1.394
45.1		1.457	1.454	1.451	1.448	1.445	1.442	1.440	1.437	1.434	1.431	1.429	1.426	1.423	1.421
46.8		1.482	1.479	1.476	1.473	1.471	1.468	1.465	1.462	1.459	1.456	1.454	1.451	1.448	1.446
48.2		1.504	1.501	1.498	1.495	1.492	1.489	1.487	1.484	1.481	1.478	1.475	1.472	1.470	1.467
51.8		1.565	1.562	1.559	1.555	1.552	1.549	1.546	1.543	1.540	1.537	1.535	1.532	1.529	1.526
53.35		1.593	1.589	1.586	1.583	1.580	1.577	1.574	1.571	1.568	1.565	1.562	1.559	1.556	1.553
55.1		1.624	1.621	1.618	1.615	1.612	1.609	1.606	1.603	1.600	1.597	1.594	1.591	1.588	1.585
55.9		1.641	1.637	1.634	1.631	1.628	1.624	1.621	1.618	1.615	1.612	1.609	1.606	1.603	1.600
57.4					1.660	1.654	1.647								
61.1			1.743	1.740	1.737	1.733	1.730	1.727	1.723	1.720	1.717	1.713	1.710	1.707	1.704
63.55						1.782	1.776		1.769		1.762		1.756		1.756

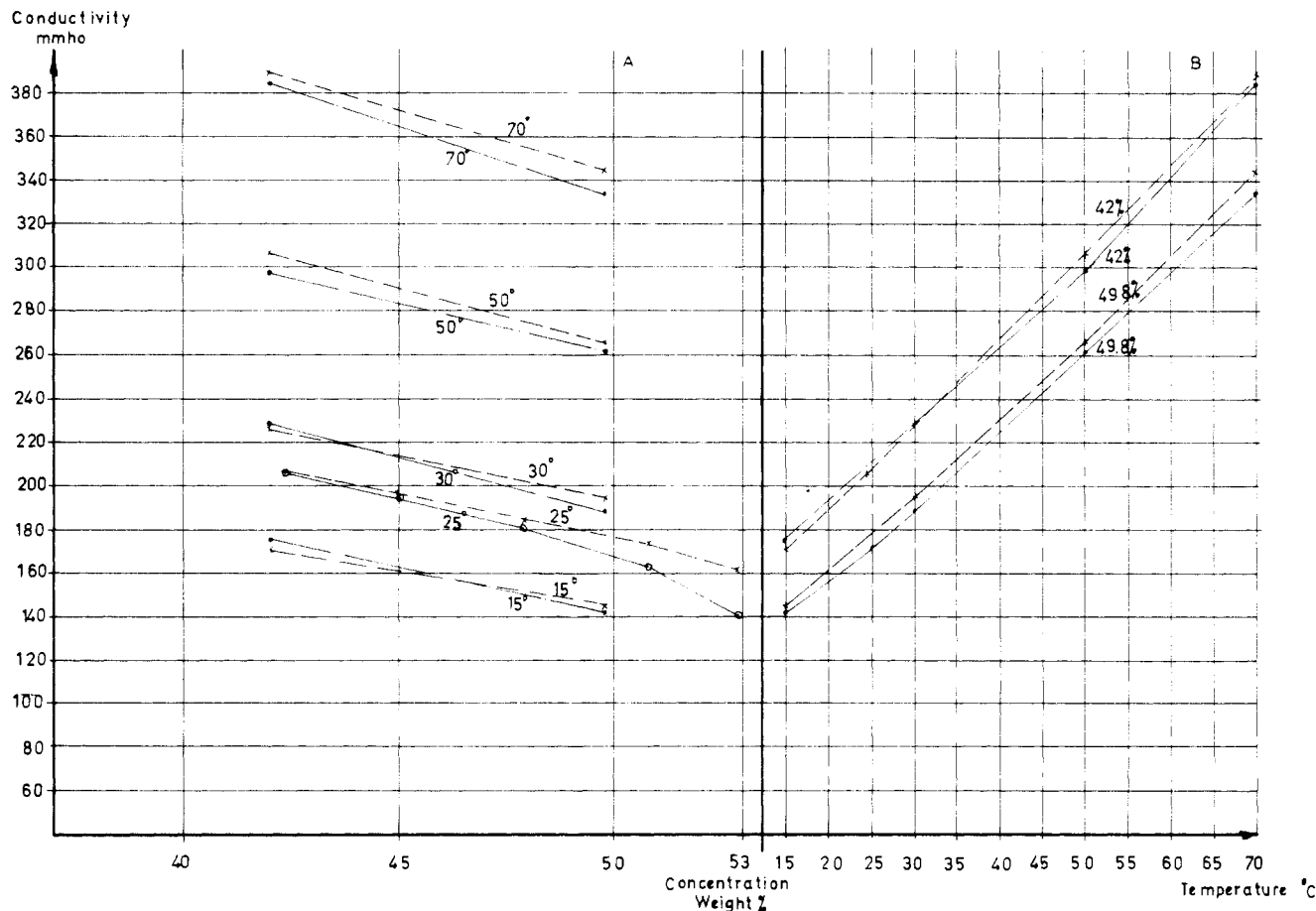


Figure 4. Comparison of results of this study (X) to those of Baron et al. (●) and Molénat (O): (A) values as a function of concentration; (B) values as a function of temperature.

as an analytical tool for absorption machines, since the concentrations of LiBr there are usually between 50 and 63 wt %.

The results obtained in this study are summarized in Figures 1–3 and in Table 1. Table II gives values for the density of the same solutions (5). Figure 1 gives the values of specific conductivity as a function of concentration in weight percent of LiBr, between 15 and 80 °C at 5 °C intervals. Figure 2 gives these values as a function of temperature and Figure 3 gives these data as a function of concentration when the latter is given in mol/L of solution). The values of concentrations in Figure 3 were obtained by the formula

$$C_M = 10dC_w/87$$

where C_M = concentration in mol/L, d = density of solution, and C_w = LiBr concentration in weight percent.

Figure 4 compares our results to those of Baron et al. and Molénat. It is apparent that the data correspond quite well to each other, even though the techniques used to measure the conductivities differed. (Baron et al. and Molénat used bridge measurement techniques.)

Acknowledgment

We thank Tadiran, Israel Electronics Industries, for permission to publish this paper.

Registry No. LiBr, 7550-35-8.

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Received for review July 7, 1980. Revised manuscript received June 4, 1982. Accepted July 31, 1982. We thank the Ministry of Industry, Commerce, and Tourism for supporting this work.