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Conductivities of Lanthanum Chloride in Water–Dimethyl Sulfoxide Mixtures at 25 °C

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The conductivities of lanthanum chloride at various concentrations in water–dimethyl sulfoxide mixtures, varying from 10.6% to 100% dimethyl sulfoxide, have been determined. The densities, viscosities, dielectric constants, and surface tensions of the various solvents have also been determined.

Introduction

In previous papers (*1*, *2*), we have dealt with the conductivities of indium chloride in water and in water–dimethyl sulfoxide mixtures and, as a standard of comparison, the corresponding data were obtained for potassium chloride. In the present study, the work has been repeated with lanthanum chloride, $LaCl_3$, as standard of reference. Lanthanum chloride is a more suitable standard of comparison than potassium chloride, since it has the same general formula as indium chloride, is a strong electrolyte, and does not suffer from hydrolysis at low concentrations of salt as indium chloride does.

In addition to determining the conductivities of lanthanum chloride solutions, we have determined the densities, viscosities, dielectric constants, and surface tensions of water-Me_2SO mixtures and have conducted thermal analysis of the system, water–Me_2SO.

Experimental Section

Materials. Lanthanum chloride was obtained from ICN Pharmaceutical Inc. It was claimed to be 99.99% but turned out to be $LaCl_3 \cdot 7H_2O$. For measurements in anhydrous Me_2SO, it was therefore necessary for us to dehydrate it and this we did by heating at 40 °C for 4 days, with continuous evacuation. Gravimetric analysis, as silver chloride, showed 98.56% $LaCl_3$. The product, on dissolving in water, showed a slight mistiness, no doubt due to the presence of La_2O_3. This material would be inert as far as conductivity is concerned but allowance was made for its effect on concentration. For solutions in water–Me_2SO mixtures, the hydrate was used, allowance being made for the water it contained.

Table I. Dielectric Constant, Density, Viscosity, and Surface Tension of Me_2SO-Water Mixtures at 25.0 °C

$[Me_2SO]$, wt %	dielectric constant	density, g/mL	η_{rel}[a]	surface tension, dyn/cm
0	78.3	0.9970	1.000	71.97
10.59	77.6	1.010	1.246	69.8
20.00	77.0	1.024	1.543	69.4
31.14	76.8	1.041	1.985	67.5
41.59	76.0	1.057	2.597	65.4
50.00	74.9	1.069	3.164	63.4
60.30	73.2	1.085	3.828	60.0
64.02		1.088	4.050	59.2
67.57		1.091	4.158	57.5
69.11	70.3	1.092	4.185	56.8
72.00		1.094	4.144	55.3
74.21		1.095	4.078	54.4
79.88	63.6	1.098	3.799	52.0
86.70		1.099	3.243	
88.00	58.0			48.5
100	44.4	1.096	2.214	42.3

[a] Relative viscosity (H_2O = 1.000).

Characteristics of the Solvents. Ordinary distilled water was passed through an ion-exchange column, which yielded water with a specific conductivity of $k = 1.0 \times 10^{-6}\ \Omega^{-1}\ cm^{-1}$. The dimethyl sulfoxide was a Fisher Certified ACS product, kept over molecular sieves (type 44, grade 514).

Procedures. The techniques of conductivity and viscosity measurements have been described in our previous publications (for instance, ref *1*). A word should be said about the determination of the surface tension. We have used the method of Sugden (*3*). The essence of this method consists in the use of two capillaries, of different bore, side by side in the same liquid. It is then only necessary to measure the difference in height of the two columns of liquid: it is not necessary to know the position of the meniscus in the outer container; this is the major uncertainty when using only one capillary.

Dielectric constants were determined by means of a Sargent oscillometer.

For the thermal analysis of the system, water–Me_2SO, ice or liquid nitrogen was used as coolant, depending on the temperature range of investigation.

Preparation of Solutions. Water–Me_2SO mixtures from 10% to 90% Me_2SO were made up by weighing. The conductivities of very dilute solutions were determined in the Shedlovsky cell, by the addition of weighed amounts of anhydrous solute. In the

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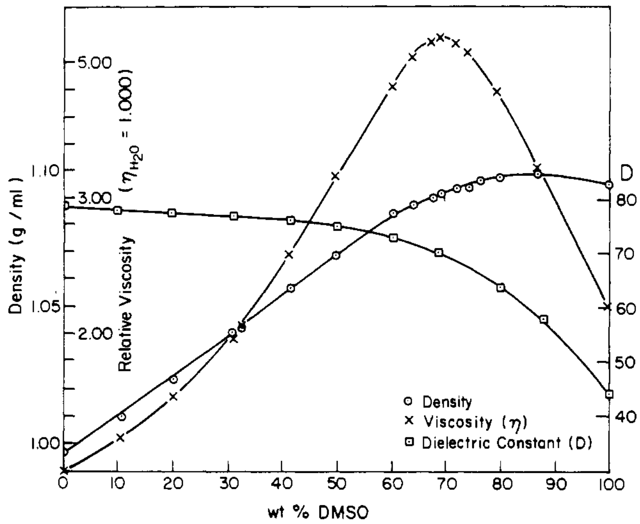

Figure 1. Densities, viscosities, and dielectric constants of Me_2SO-water mixtures at 25.0 °C.

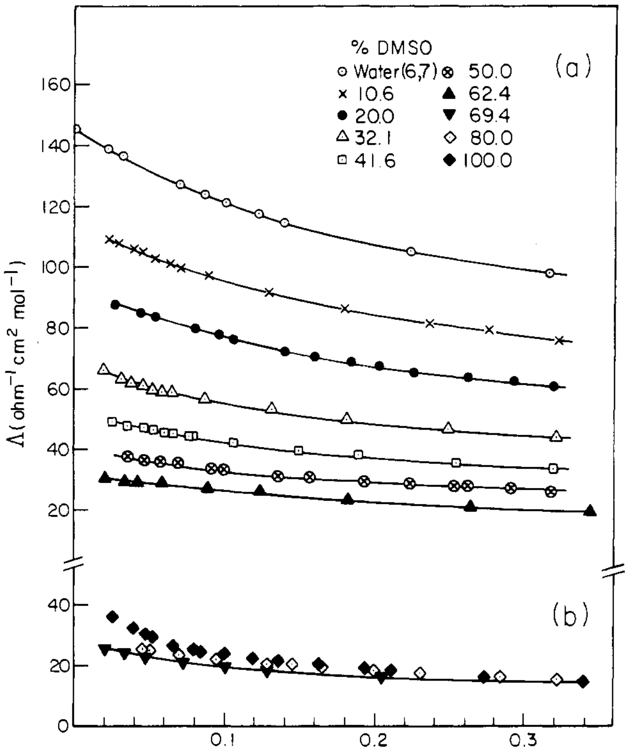

Figure 2. (a and b) Λ vs. $c^{1/2}$ for $LaCl_3$ in Me_2SO-water mixtures at 25.0 °C. The ordinate has been split in order to avoid confusion around the minimum at 70% Me_2SO.

range 0.005–0.1 M, solutions were made by dilution of a 0.1 M solution ($^1/_3$ $LaCl_3$).

Results

Densities, viscosities, dielectric constants, at 25 °C, of water-Me_2SO mixtures are given in Table I and are plotted in Figure 1. Surface tensions are also given in Table I.

The conductivities, specific and molar, are given in Table II and expressed graphically in Figures 2 and 3 in the form of Λ vs. $c^{1/2}$ ad $\Lambda\eta$ vs. $c^{1/2}$.

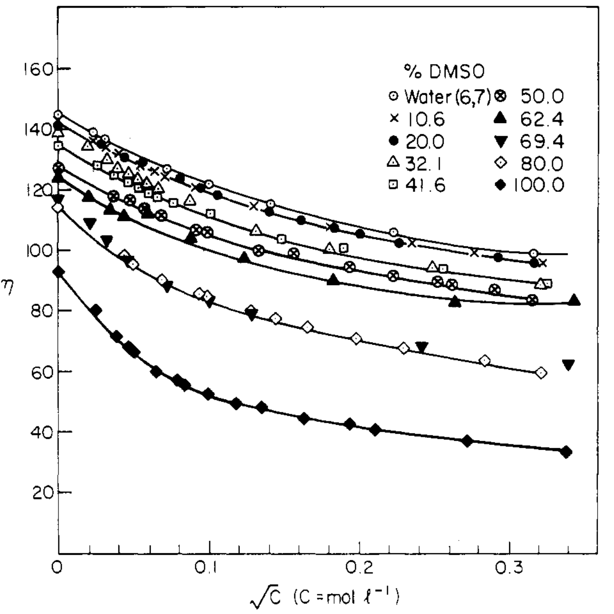

Figure 3. $\Lambda\eta$ vs. $c^{1/2}$ for $LaCl_3$ in Me_2SO-water mixtures.

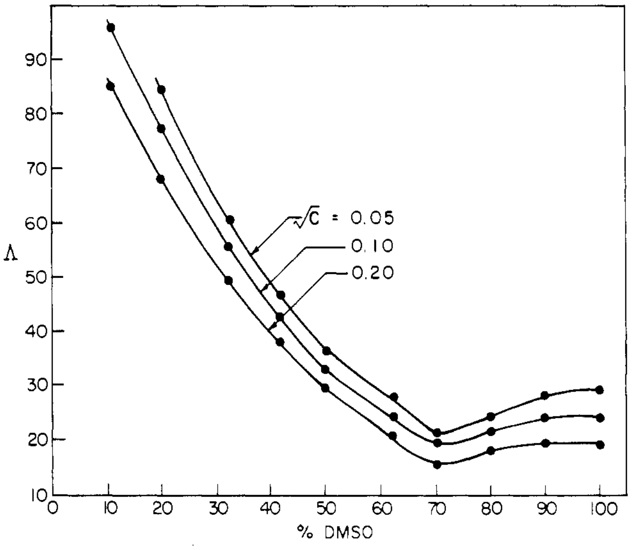

Figure 4. Λ vs. wt % Me_2SO for constant concentrations of $LaCl_3$ ($c^{1/2}$ = 0.05, 0.10, 0.20).

In the thermal analysis, when Me_2SO was the solid phase separating, we were unable to obtain satisfactory freezing points because of supercooling, but every mixture in the composition range from 8.9% to 82.2% water yielded the same strongly marked eutectic at 29 °C. The system containing 31% water exhibited the eutectic halt only and therefore has the eutectic composition.

Discussion

Inspection of Figure 1 shows that the density passes through a flat maximum between 80 and 90 wt % Me_2SO. The viscosity curve exhibits a very pronounced maximum at 70 wt % Me_2SO. Morel (*4*) summarizes the properties of Me_2SO-water mixtures: quoting the results of Cowie and Toporowski (*5*), he points to the pronounced maximum on the viscosity-concentration curve, which occurs at a concentration corresponding to the formula $Me_2SO{\cdot}2H_2O$ (68.4%). Morel suggests that a complex of this type may exist in solution. The results of thermal analysis show only one eutectic and therefore this hypothetical compound does not exist in the solid state although it may exist in solution.

When the surface tension values are plotted against weight percent or mole percent, smooth curves are produced without maxima or minima.

As for the conductivity results, Figure 2 shows a decrease in Λ with increasing Me_2SO content to 70% Me_2SO, followed by a slight increase in conductivity to 100% Me_2SO. In order

Table II. Conductivities and $\Delta\eta$ of Lanthanum Chloride in Water-Me_2SO Mixtures at 25.0 °C

c,[a] M	$c^{1/2}$	10^5k, Ω^{-1} cm^{-1}	Λ, Ω^{-1} cm^2 mol^{-1}	$\Lambda\eta$
1. 10.6% Me_2SO (η_{rel} = 1.246, (H_2O) = 1)				
0.000 5351	0.0231	5.86	109.6	136.7
0.000 9724	0.0312	10.5	108.2	134.9
0.001 575	0.0397	16.7	106.0	132.2
0.002 047	0.0452	21.5	105.2	131.1
0.002 997	0.0547	30.8	102.9	128.4
0.004 063	0.0637	41.1	101.2	126.2
0.005 029	0.0709	50.2	99.8	124.5
0.008 510	0.0922	82.8	97.3	121.3
0.017 00	0.1304	156.8	92.2	114.9
0.032 9	0.181	285.1	86.7	108.0
0.055 8	0.236	458.6	82.2	102.4
0.076 7	0.277	611.3	79.7	99.3
0.104 5	0.323	803.1	76.9	95.8
2. 20.0% Me_2SO (η_{rel} = 1.543)				
0.000 7856	0.0280	6.43	87.9	135.6
0.002 024	0.0450	17.26	85.3	131.6
0.003 131	0.0560	26.2	83.7	129.1
0.006 594	0.0812	52.9	80.3	123.9
0.008 965	0.0947	70.1	78.2	120.7
0.011 15	0.1056	85.4	76.6	118.2
0.019 50	0.1397	141.9	72.8	112.3
0.026 3	0.162	187.0	71.0	110.0
0.033 8	0.184	235.0	69.5	107.2
0.041 0	0.203	279.0	68.1	105.0
0.051 0	0.226	338.0	66.3	102.3
0.068 8	0.262	445.0	64.7	99.8
0.085 6	0.293	540.0	63.1	97.4
0.100 9	0.318	623.0	61.8	95.3
3. 32.1% Me_2SO (η_{rel} = 2.043)				
0.000 4095	0.0202	2.71	66.1	135.0
0.001 005	0.0317	6.40	63.7	130.1
0.001 525	0.0390	9.52	62.4	127.6
0.002 199	0.0469	13.5	61.5	125.6
0.002 785	0.0528	16.9	60.6	123.8
0.003 521	0.0593	21.1	59.9	122.4
0.004 414	0.0664	26.0	59.0	120.5
0.007 51	0.0866	42.9	57.1	116.7
0.017 15	0.131	92.0	53.7	106.5
0.032 94	0.181	166.4	50.5	100.2
0.061 87	0.249	293.4	47.4	94.1
0.103 9	0.322	466.5	44.9	89.1
4. 41.6% Me_2SO (η_{rel} = 2.597)				
0.000 6656	0.0258	3.29	49.4	128.4
0.001 390	0.0373	6.70	48.2	125.1
0.002 161	0.0465	10.2	47.2	122.5
0.002 848	0.0534	13.3	46.5	120.8
0.003 550	0.0596	16.3	45.9	119.3
0.004 315	0.0657	19.6	45.4	117.9
0.005 963	0.0772	26.5	44.5	115.6
0.006 576	0.0811	29.6	45.0	116.7
0.011 49	0.1072	49.2	42.8	112.2
0.022 2	0.149	88.8	40.0	103.8
0.036 45	0.190	141.5	38.8	100.8
0.065 56	0.256	237.7	36.3	94.2
0.105 0	0.324	359.4	34.2	88.9
5. 50.0% Me_2SO (η_{rel} = 3.164)				
0.001 318	0.0363	4.94	37.5	118.7
0.002 184	0.0467	8.04	36.8	116.5
0.003 390	0.0582	12.2	36.0	114.0
0.004 744	0.0689	16.8	35.3	111.7
0.008 473	0.0920	28.7	33.9	107.2
0.009 717	0.0986	32.6	33.6	106.3
0.018 11	0.135	57.4	31.7	100.3
0.024 70	0.157	77.4	31.4	99.2
0.037 49	0.194	112.3	30.0	94.8
0.050 01	0.224	145.2	29.0	91.9
0.064 24	0.253	181.7	28.3	89.5
0.068 36	0.261	191.5	28.0	88.7
0.084 64	0.291	233.0	27.5	87.0
0.100 4	0.317	266.2	26.5	83.9
6. 62.4% Me_2SO (η_{rel} = 3.828)				
0.000 4279	0.02069	1.32	30.8	117.9
0.001 201	0.03465	3.57	29.7	113.7
0.001 925	0.04387	5.60	29.1	111.4
0.003 615	0.0601	10.6	29.3	112.2
0.007 75	0.0882	21.1	27.2	104.3
0.015 38	0.124	39.2	25.5	97.5
0.034 49	0.183	78.6	23.5	89.8
0.069 90	0.264	150.3	21.5	82.3
0.119 0	0.345	240.8	20.2	83.2
7. 69.4% Me_2SO (η_{rel} = 4.199)				
0.000 4308	0.020 76	1.12	26.0	109.2
0.001 090	0.0331	2.68	24.6	103.4
0.002 20	0.0469	5.05	23.0	96.4
0.005 166	0.0719	10.9	21.1	88.3
0.010 23	0.1012	20.2	19.8	83.0
0.016 39	0.128	31.0	18.7	79.4
0.058 69	0.242	95.5	16.3	68.3
0.115 5	0.3398	171.1	14.8	62.2
8. 80.0% Me_2SO (η_{rel} = 3.799)				
0.002 052	0.0453	5.31	25.89	98.4
0.002 499	0.0500	6.28	25.15	95.5
0.004 900	0.0700	11.61	23.69	90.0
0.008 95	0.0946	20.09	22.44	85.3
0.009 99	0.0999	21.86	22.18	84.3
0.016 77	0.129	34.93	20.83	79.1
0.021 0	0.145	42.83	20.31	77.2
0.027 4	0.166	53.63	19.57	74.4
0.039 7	0.199	74.15	18.70	70.7
0.040 2	0.201	74.73	18.59	70.6
0.053 1	0.230	94.72	17.83	67.7
0.080 9	0.284	134.8	16.66	63.3
0.104 2	0.3227	162.8	15.62	59.4
9. 90% Me_2SO (η_{rel} = 3.060)				
0.002 544	0.05044	7.40	29.10	89.0
0.009 754	0.09876	24.0	24.60	76.2
0.039 99	0.1999	79.34	19.84	60.7
10. 100% Me_2SO (η_{rel} = 2.214)				
0.000 613	0.0248	2.22	36.2	80.1
0.001 486	0.0386	4.82	32.5	71.9
0.002 25	0.0474	6.91	30.7	68.0
0.002 48	0.0498	7.47	30.1	66.6
0.002 66	0.0516	7.93	29.9	66.1
0.004 19	0.0647	11.4	27.1	60.0
0.004 21	0.0649	11.2	26.6	58.9
0.006 21	0.0788	16.0	25.8	57.1
0.007 11	0.0843	17.7	24.9	55.1
0.009 99	0.0999	23.9	23.9	52.9
0.013 9	0.118	31.0	22.3	49.4
0.018 3	0.135	39.9	21.8	48.2
0.026 5	0.163	53.3	20.1	44.5
0.037 6	0.194	72.7	19.3	42.8
0.044 4	0.211	81.4	18.4	40.7
0.074 3	0.273	124.2	16.7	37.0
0.114 1	0.338	173.6	15.2	33.7

[a] $^1/_3$ $LaCl_3$.

to make this clearer, Figure 4 shows the change in Λ with Me_2SO content for fixed concentrations of lanthanum chloride ($c^{1/2}$ = 0.05, 0.10, and 0.20). There is a slight but real minimum at 70% Me_2SO, at which concentration there is a maximum in the viscosity curve. The curves of Figure 2 were extrapolated to $c^{1/2}$ = 0 and the slopes determined. These data are given in Table III. The experimental slopes decrease progressively to between 60% and 70% Me_2SO and then increase. This presumably is the result of the decrease in viscosity beyond 70% Me_2SO. Table III also has a column, headed $\Lambda\eta(c^{1/2}=0)$, where the limiting Λ has been multiplied by the viscosity of the solvent. These values are essentially

Table III. Molar Conductivities of Lanthanum Chloride Extrapolated to $c^{1/2} = 0$ in Me_2SO-Water Mixtures and Limiting Experimental Slopes of Λ vs. $c^{1/2}$

$[Me_2SO]$, wt %	$\Lambda(c^{1/2}=0)$	$\Lambda\eta(c^{1/2}=0)$	slope-$(c^{1/2}=0)$
0	145.8	145.8	282
10.6	114.6	142.8	172
20.0	92.0	142.0	146
32.1	68.6	140.1	133
41.6	52.0	135.0	86
50.0	40.1	126.9	62
62.4	32.5	124.4	56
69.4	28.0	117.6	81
80.0	30.0	114.0	78
100.0	42.0	93.0	181

constant up to about 30% Me_2SO, where the dielectric constant is about 55.

If the conductivities of indium chloride (*2*) are compared with those of lanthanum chloride, at the same concentrations of salt and Me_2SO, those of indium chloride are seen always to be lower than those of lanthanum chloride, except in the region where hydrolysis of indium chloride occurs, that is, in dilute solutions in water-rich solvent. There is no minimum in a plot of Λ vs. Me_2SO content for fixed indium chloride content, as there is in the case of lanthanum chloride (Figure 4). The occurrence of the minimum in the latter is probably due to the decrease in the viscosity of the solvent at Me_2SO concentrations greater than 70%. The absence of a minimum in the case of indium chloride may be due to an increasing number of nonconducting ion associates in this region.

Registry No. $LaCl_3$, 10099-58-8; Me_2SO, 67-68-5.

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Vapor-Liquid Equilibrium in the System 2-Propanol-Isopropylbenzene

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New vapor-liquid equilibrium data have been measured for the binary system 2-propanol-isopropylbenzene at 760 mmHg and compared with previously reported data which are suspected to be thermodynamically inconsistent. The system presents strong positive deviations from ideal solution behavior. The activity coefficients are well correlated by a three-constant Redlich-Kister equation and by the Wilson equation. Boiling points are adequately described by two different equations.

Introduction

Kumar and Raju (*1*) have recently reported vapor-liquid equilibria data for the systems 2-propanol-isopropylbenzene and allyl alcohol-isopropylbenzene at 760 mmHg. They analyzed the thermodynamic consistency of the data using the criteria of Herrington (*2*), Norrish-Twigg (*3*), and Black (*4*, *5*), apparently by estimating the necessary thermal data. On the basis of these methods they claim that the data are consistent in spite of the fact that the areas under the curves log γ_i against composition are substantially different. In addition, the system allyl alcohol-isopropylbenzene presents positive deviations from ideal behavior for the alcohol and negative deviations for the hydrocarbon.

Solutions of alcohols are known to deviate strongly from ideal behavior (*6*-*8*). For aromatic hydrocarbons the analysis of the thermodynamic and spectroscopic data has suggested that the π electrons and the proton of the hydroxyl group interact strongly (*7*). Hwa and Ziegler (*6*) developed a more complicated model which assumed an additional interaction between the aromatic ring and alcohol polymeric species which does not require breaking of the hydrogen bonds. Van Ness et al. (*8*) have reported the excess mixing properties for several alcohol-hydrocarbon systems.

Table I. Physical Constants of Pure Compounds

index	compd	refractive index at 25 °C	bp(760 mmHg), °C	% purity GLC (min)
1	2-propanol	1.3756[a] 1.3752[b]	82.30[a] 82.26[b]	99.5
2	isopropylbenzene	1.4890 1.4889[b]	152.3[a] 152.39[b]	99.3

[a] Measured. [b] Reference *14*.

The system discussed in this work cannot exhibit the required large thermal effects to justify the observed inconsistency in the Kumar and Raju data; instead, it must be due to data of poor quality. We have measured the vapor-liquid equilibrium at 760 mmHg to verify our assumptions.

No additional data are available for further comparison.

It should be mentioned that the behavior reported by Kumar and Raju has also been observed by Chandrashekara and Seshadri (*9*) for the system methyl ethyl ketone-*p*-xylene. Our measurements (*10*) have pointed out that in the latter the inconsistency was also due to data of poor quality.

Experimental Section

Purity of Materials. Analytical-grade reagents purchased from Fluka were used without further purification. Gas chromatography analysis failed to show any significant impurities. Physical properties of the pure components appear in Table I.

Apparatus and Procedure. An all-glass modified Dvorak and Boublik recirculation still (*11*) was used in the equilibrium de-