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Relative Apparent Molar Enthalpies of Aqueous Lanthanum Perchlorate

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Relative apparent molar enthalpies (ϕ_L) were measured at 25°C for lanthanum perchlorate solutions over the molality range 0.004–4.74*m*. The results were fitted to a Debye-Hückel equation for smoothing and extrapolation to $m = 0$.

Previous measurements (*3, 8, 9*) of relative apparent molar enthalpies (ϕ_L) for $HClO_4$, $NaClO_4$, $Mg(ClO_4)_2$, $Sr(ClO_4)_2$, and $Ba(ClO_4)_2$ yielded ϕ_L values which could be fitted to 0.4*m* or higher with an equation based on the Debye-Hückel theory, and thereby could be extrapolated reliably to the standard reference state $m = 0$. For a 3-1 perchlorate free from hydrolysis effects, $La(ClO_4)_3$ was chosen as a suitable convenient substance for this study. Since the ion is isoelectronic with that of barium, the effect of increased cationic charge would be revealed for the multiply charged ions.

Experimental

Materials. Freshly distilled water, collected at about 75°C, was used for all solutions and in all of the dilution measurements.

Preparation of the $La(ClO_4)_3$ solutions followed the method of Roberts and Silcox (*6*). An excess of lanthanum oxide (Matheson Coleman & Bell; purity 99.99%) was slurried with distilled water, and AR perchloric acid (Baker and Adamson, 60% $HClO_4$) was added slowly with stirring until most of the La_2O_3 was dissolved. The mixture was heated to about 90°C, with constant stirring, for 24 hr, after which the mixture was cooled and filtered through a Buchner funnel with a 1-cm thick asbestos mat. A second filtering, either through a similar mat or through filter paper, was done to ensure removal of colloidal solid. No Tyndall effect was observed on the resulting solutions. The pH of the solutions was adjusted to between 5 and 6 with small amounts of $HClO_4$, and the concentrations of the solutions were then increased as needed by evaporation at 90–100°C.

The stock solutions were analyzed by precipitating the lanthanum as the oxalate, which was then converted to La_2O_3 by ignition for 5 hr at 850°C in a muffle furnace (*4*). Analytical precision for triplicate analyses was generally better than 0.05% for the ratio (mass of $La(ClO_4)_3$/mass of solution). All weighings of solutions and solids were appropriately reduced to masses, with densities from literature sources (*2, 6*). Nine different solutions were analyzed. Other solutions of intermediate concentrations were prepared by mass dilutions from analyzed stock solutions and freshly distilled water.

Calorimetric equipment and procedures. The configuration of the solution calorimeter used in this work was that described previously (*8*), and these measurements on $La(ClO_4)_3$ occurred in the same time period as those on $HClO_4$ and $NaClO_4$. The first 18 dilution runs were made with the Maier transposed bridge (*8*), with a temperature sensitivity of $\pm 5 \times 10^{-5}$ K, except for a few dilution runs at a sensitivity of $\pm 2 \times 10^{-5}$ K. The remaining dilution runs with thermistor bridge circuits (*8*) were made with a sensitivity of $\pm 1.5 \times 10^{-5}$ K. The electrical energy equivalents are considered accurate to ±0.02%. The isothermal jacket (bath) was controlled to ±0.003K during this work.

Corrected temperature increments were evaluated by Dickinson's method (*1*). Temperature-time data for 10-minute fore and after periods were fitted by least squares, and "midtimes" were determined by detailed examination of typical temperature-time curves for dilution and electrical calibration measurements. Main periods were sufficiently long (4–6 min plus duration of the mixing or calibration period) to allow attainment of equilibrium drift rates in the after period. Dilutions were initiated at 25.00 ± 0.02°C, and electrical calibrations were made on the final state of the system.

The pattern for dilution measurements was that used in the previous studies (*8, 9*), with about 1.05 liters of water or dilute $La(ClO_4)_3$ of measured mass in the calorimeter vessel, and with the 39-ml dilution capsule filled with a measured mass of concentrated solution, molality *m*. The general process is:

$$La(ClO_4)_3(m_0) + rLa(ClO_4)_3(m_1) = (1 + r)\ La(ClO_4)_3(m_2) \qquad (1)$$

where r (and m_1) are zero for the first step in a series (dilution into water). Several such series were run, with up to six steps in a series, plus a substantial number of single-step runs. For each step, the enthalpy change is

$$\Delta H = (1 + r)\ (\phi_2 - \phi_0) - r(\phi_1 - \phi_0) \qquad (2)$$

where ϕ is the apparent molar enthalpy referred to an arbitrary zero point, and the subscripts identify the particu-

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Table II. Relative Apparent Molar Enthalpies at 25°C for Lanthanum Perchlorate at Experimental Molalities[a]

m, mol kg^{-1}	ϕ_L, exp, cal mol^{-1}	ϕ_L, calc, cal mol^{-1}	m, mol kg^{-1}	ϕ_L, exp, cal mol^{-1}	ϕ_L, calc, cal mol^{-1}
0.003945	318	322	0.1108	...	769
0.01202	472	470	0.1234	780	779
0.01705	521	521	0.1275	782	782
0.02147	558	555	0.1456	793	793
0.02712	586	589	0.1460	792	793
0.03152	...	610	0.1896	813	810
0.03317	...	618	0.2155	818	817
0.03417	623	622	0.2846	826	827
0.03697	628	633	0.3521	826	828
0.04151	647	649	0.4895	829	829
0.04318	651	654	0.6388	830	833
0.05037	675	675	0.8082	865	857
0.05455	689	686	0.9618	893	890
0.05649	...	691	0.9973	890	900
0.06446	698	707	1.1280	953	955
0.06602	...	711	1.306	1073	1065
0.07361	726	724	1.620	1290	1285
0.07375	729	724	1.903	1565	1595
0.07387	724	724	2.188	1950	2010
0.07835	...	731	2.244	2134	2100
0.08376	739	739	2.640	2794	2795
0.08754	...	744	2.871	3240	3200
0.09690	756	754	3.201	3820	3830
0.09903	759	758	3.604	4611	4620
0.1012	...	759	3.978	5416	5425
0.1064	...	765	4.383	6355	6350
0.1099	...	769	4.675	7093	7020
0.1100	772	769	4.737	7151	7160
0.1103	...	769	4.737	7162	7160

[a] Experimental molalities, m, corresponding to Table I. Values of ϕ_L, exp, are based on interlocking groups of values forming an arbitrary curve which was extrapolated by the Debye-Hückel equation. Values of ϕ_L, calc, are based on the Debye-Hückel equation up to m = 0.3 mol kg^{-1} and above that molality are taken from large-scale graphs.

Table III. Selected Values of Relative Apparent Molar Enthalpies of Lanthanum Perchlorate Solutions at 25°C

n (H_2O)	m, mol kg^{-1}	ϕ_L, cal mol^{-1}	n (H_2O)	m_1, mol kg^{-1}	ϕ_L, cal mol^{-1}
∞	0	0	150	0.3700	828
555,060	0.000100	66	111	0.5000	829
500,000	0.000111	69	100	0.5551	830
200,000	0.000278	107	75	0.7401	845
100,000	0.000555	145	55.51	1.0000	900
55,506	0.001000	187	50	1.1101	944
50,000	0.001110	196	40	1.3877	1118
22,202	0.002500	272	37	1.5000	1195
20,000	0.002775	283	30	1.8502	1540
10,000	0.005551	363	27.75	2.0000	1730
7500	0.007401	400	25	2.2202	2060
5551	0.01000	443	20	2.775	3030
5000	0.01110	458	18.5	3.000	3460
3000	0.01850	533	17	3.265	3950
2000	0.02775	592	15	3.700	4830
1000	0.05551	688	13.88	4.000	5460
800	0.06938	716	13	4.270	6060
555	0.1000	759	12.5	4.440	6480
500	0.1110	769	12.33	4.500	6600
300	0.1850	808	12	4.626	6920
200	0.2775	825	11.69	4.750	7200

lar solution. Each series yields a set of arbitrary values forming a segment of a curve of ϕ_i vs. $m^{1/2}$. These segments were blended into a single curve by appropriate scaling adjustments of the ϕ_0 values, after which individual runs were fitted into the curve.

The composite arbitrary curve was then fitted to the Debye-Hückel function previously described (*5*, *8*) by a combination of graphical and computer techniques. The ion-size parameter, a = 0.64 nm, was selected from the work of Spedding and Jaffe (*7*) on several trivalent rare earth perchlorates. The remaining adjustable parameters are: the temperature coefficient $(\partial \ln a/dT)_p$; b, the coefficient of a term linear in molality; and $\phi°$, the apparent molar enthalpy at infinite dilution. The equation was applied in terms of molalities rather than concentrations.

The values $(\partial \ln a/\partial T)_p = 2.5 \times 10^{-4}$ K^{-1} and b = 270 cal kg^{-1} mol^{-2} gave best fit over the molality range 0–0.4m. For variations of ±0.04 nm in a, with compensating adjustments in the other parameters, the intercept $\phi°$ at $m = 0$ was constant to ±5 cal mol^{-1}, but with significant reduction in the molality range that could be fitted. The intercept value $\phi°$ was used with the equation over its applicable range to generate smoothed values of the relative apparent molar enthalpy, $\phi_L = \phi - \phi°$, and to adjust the reference point of the experimental ϕ_i curve to give experimental values of ϕ_L. Values of ϕ_L at selected molalities above the range of fit were taken from large-scale plots of the experimental values.

Results and Discussion

Table I (deposited with the ACS Microfilm Depository Service) contains the primary experimental data related to Reaction 1. Table II presents observed values of ϕ_L at experimental molalities, together with smoothed values for comparison. Table III presents selected values of ϕ_L at selected molalities and mole ratios.

The accuracy of the experimental results can be seen from comparison of ϕ_L, exp, and ϕ_L, calc, for values given in Table II. In the range of molalities below 1m, the predominant source of error is in the calorimetry, in measurement of the corrected temperature rise. Above 1.3m, the predominant source of error is in the analysis of the solutions and subsequent magnification of the analytical error in computing molality. In this region where ϕ_L increases rapidly with m, deviations from plots of ϕ_L against m are, for a given analytical error, up to four times as great on the m-axis as in ϕ_L. The point at 4.675m probably includes a substantial calorimetric or manipulative error which could not be located and was given little weight in the final adjusted results. The overall uncertainty in $\phi°$ in extrapolation was judged to be ±15 cal mol^{-1}, and the overall uncertainty in ϕ_L was judged to be 3% of ϕ_L or 25 cal mol^{-1}, whichever is the smaller quantity.

For $Ba(ClO_4)_2$, the values of ϕ_L reached a maximum at about 0.06m and decreased to large negative values near saturation conditions. In contrast, the values for $La(ClO_4)_3$ rise go to an almost horizontal inflection point near 0.4m, and above 1.5m rise rapidly to large positive values at high molalities. This latter rise appears to be characteristic of substances with strongly hydrated cations. Close inspection of the trend of density with molality (*6*) reveals a change in the trend around 1.5m for this property also.

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Velocity of Sound in Binary Mixtures of Benzene, Hexane, and Methanol at 0–65°C

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Sound velocities and densities of liquid hexane, benzene, methanol, and a number of binary solutions were measured over the temperature range from 0° to 65°C. The sound velocities were scaled from photographic records provided by a pulse-echo instrument by using a 1-MHz quartz crystal. The sound velocity isotherms of the nonideal binary mixtures exhibited minima, whereas those for the ideal mixture were slightly curved. The densities varied linearly with temperature. Adiabatic compressibilities, ratio of heat capacities, and the heat capacity at constant volume were calculated. The results were in general agreement with available experimental and theoretical values in the literature.

Considerable scientific and practical interest has been stimulated by the investigation of organic solutions with ultrasonic measurements. Important physicochemical properties of solutions, such as adiabatic and isothermal compressibilities, ratio of heat capacities (C_p/C_v), heat capacity at constant volume (C_v), coefficient of expansion, and critical temperature, may be determined from ultrasonic velocity and density data.

Most previous investigations, e.g., methyl and ethyl alcohol in carbon tetrachloride (*5*), n-hexane in methanol (*14*), fluorocarbons (*7*), alcohols (*8*), benzene in nitrobenzene (*16*), aniline in n-hexane and triethylamine–H_2O (*2*), and aniline–cyclohexane (*1*), have been limited to narrow temperature ranges. Nozdrev's (*9*) investigation of benzene, toluene, and methylxylene in carbon tetrachloride and Marks' (*8*) investigation of alcohol mixtures initiated the systematic study of solutions based upon ultrasonic velocity data. Additional systematic investigations of solutions by ultrasonic velocity data are needed to elucidate the liquid state and correlate mixing rules.

This paper presents data from a systematic study of sound velocity as a function of composition for the binary mixtures of benzene, methanol, and hexane over a temperature range of 0–65°C.

Experimental

Measurements of sound velocity were made at 1 MHz by the pulse echo method (*15*) by using an electronic pulser coupled to a high gain amplifier (*13*). The oscilloscope trace of the echoes was photographed, and the time between successive echoes was scaled to ±0.2 μ sec on a microscope equipped with a movable Lafayette mechanical stage. A standard time signal (Micro-Marker) was superimposed on the oscilloscope trace and used to correct for nonlinear amplification of the high gain amplifier and oscilloscope. Velocity data were calculated from the time between two successive echoes and the distance between the barium titanate transducer and the nickel reflector. Parallelism of the reflector and transducer was maintained by three adjustment screws on the reflector. The liquid sample chamber containing the reflector and transducer was immersed in a constant tempera-

Table I. Least-Squares Coefficients for Pure Component Relations

Polynomial coefficients of density in g/cm³ for $\rho = A + Bt$ with t = °C

Polynomial degree	Component	$A \times 10^{+1}$	$B \times 10^{+3}$	SD	No of points
		Density–temperature			
1	Benzene	9.0000	−1.0597	2.96×10^{-4}	15
1	Methanol	8.104229	−0.93779	2.38×10^{-3}	14
1	Hexane	6.799439	−0.90556	1.14×10^{-3}	14

Polynomial coefficients of sound velocity in m/sec for $C = A + Bt$ with t = °C

Polynomial degree	Component	$A \times 10^{-3}$	$A \times 10^{0}$	SD	No. of points
		Sound velocity–temperature			
1	Benzene	1.37798	−4.4490	4.67	30
1	Methanol	1.14909	−2.9223	4.73	14
1	Hexane	1.15818	−4.31796	2.32	36

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