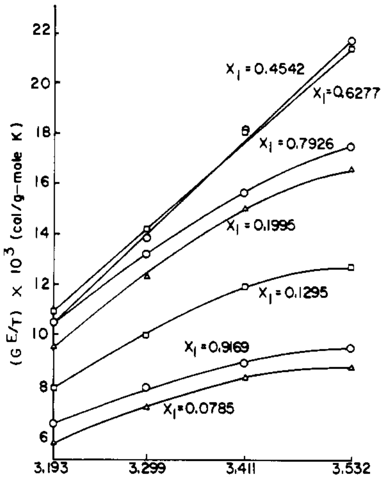

Figure 4. g^E/T vs. $1/T$ for *n*-hexane–3-methylpentane at various hexane mole fractions.

0.1-mm random pressure error. The derived values of h^E and Ts^E are considerably less reliable.

Glossary

A, B, C	constants in expansions of g^E
g^E	excess Gibbs free energy, cal/mol
h^E	excess enthalpy, cal/mol
P	total pressure, mmHg
P_1, P_2	vapor pressures of components 1 and 2, mmHg
v	molar volume, mL
x	mole fraction in liquid
y	mole fraction in vapor

Greek Letters

β	virial coefficients
δ	defined by eq 9
γ	activity coefficient

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Infinite Dilution Activity Coefficients for Selected Binary Mixtures of Hydrocarbons, Alcohols, and Ketones

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Infinite dilution activity coefficients are determined in a gas–liquid partition chromatograph of a new design. Data are reported for 2-pentanone and 1-pentanol as solutes in 1-methylnaphthalene and phenanthrene, 2-nonanone in phenanthrene, and various hydrocarbons in 2-nonanone and 1-hexadecanol. Temperatures observed include 60, 120, and 180 °C.

Infinite dilution activity coefficients of solutes in pure solvents are of much interest in solution thermodynamics. They define boundary conditions in the integration of the Gibbs–Duhem equation and are the most sensitively reflective of the departures of the solutes from ideal solution behavior. Schreiber and Eckert (*4*) showed that the real solution behavior in the complete composition range can be described on the basis of data on the infinite dilution activity coefficients only.

The experimental apparatus and procedure of this work have been described (*5*). Briefly the apparatus is a gas–liquid partition chromatograph of a new design for the accurate determination of the gas–liquid vaporization equilibrium ratio K of the solute at infinite dilution over a wide temperature range. The infinite dilution activity coefficient γ^∞ is calculated from the K^∞ value. K_a^∞ is defined as the limit of y_a/x_a as x_a approaches zero, where y_a and x_a are mole fractions of component a in the vapor and liquid, respectively.

Table I. Chemicals Used in This Work

substance	source	% purity
helium	Airco (purified, grade 4.5)	99.9/95
n-hexane	Phillips, Research Grade	99.96
1-pentanol	Eastman	99
1-hexadecanol	Baker Chemicals[a]	99
2-pentanone	Aldrich	97
2-nonanone	Aldrich	99.5
benzene	Phillips, Research Grade	99.9
toluene	Phillips, Research Grade	99.4
ethylbenzene	Phillips, Research Grade	99.9
n-propylbenzene	Aldrich	98
p-xylene	Phillips, Research Grade	99.9
naphthalene	Fisher, certified	99+
1-methylnaphthalene	Aldrich[a]	99
phenanthrene	Eastman[b]	99

[a] Purified by fractional distillation. [b] Recrystallized in ether.

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Table II. Infinite Dilution K Values and Activity Coefficients in 1-Methylnaphthalene

$T_{col} = 120.0$ °C, $p_{col} = 42.7$ psia

solute	K^∞	p°(solute), atm	ϕ°(solute)	Poynting term	γ^∞(solute)
2-pentanone	0.7126	2.990	0.8795	.9997	0.788
1-pentanol	0.4890	0.5429	0.9663	1.0074	2.69

Table III. Infinite Dilution K Values and Activity Coefficients in Phenanthrene

solute	K^∞	p°(solute), atm	ϕ°(solute)	Poynting term	γ^∞(solute)
		$T_{col} = 120.0$ °C, $p_{col} = 48.0$ psia			
2-pentanone	0.6485	2.990	0.8795	1.0009	0.805
1-pentanol	0.4665	0.5428	0.9663	1.0085	2.88
		$T_{col} = 180.0$ °C, $p_{col} = 47.8$ psia			
2-pentanone	1.936	10.56	0.8295	0.9786	0.735
1-pentanol	2.033	3.318	0.9286	0.9998	2.15
2-nonanone	0.2822	0.7212	0.9700	1.0137	1.29

Table IV. Infinite Dilution K Values and Activity Coefficients in 2-Nonanone

$T_{col} = 60.0$ °C, $p_{col} = 53.7$ psia

solute	K^∞	p°-(solute), atm	ϕ°-(solute)	Poynting term	γ^∞-(solute)
n-hexane	0.3791	0.7537	0.9645	1.0139	1.88
benzene	0.1320	0.5150	0.9755	1.0115	0.948
toluene	0.04945	0.1828	0.9829	1.0141	0.991

The simplified form of relation of retention time to vapor–liquid equilibrium can be written in terms of quantities measured in this experimental work as

$$K_A^\infty = \frac{m_s W_{He}(p - p_s^\circ)}{W_s p F_0(t_{R_A} - t_g)} \quad (1)$$

where $K_A^\infty = y_A/x_A$ the equilibrium ratio of solute A, m_s is the mass of stationary phase coated on the column packing material, W_{He} is the molecular weight of the carrier gas, W_s is the molecular weight of the stationary liquid, p is the pressure in the partition column, p_s° is the vapor pressure of the stationary liquid at the column temperature, F_0 is the mass flow rate of the carrier gas, t_{R_A} is the retention time of solute A, and t_g is the retention time of a hypothetical insoluble gas. t_g is approximated in this work as the retention time of argon and is small compared to t_{R_A}.

$$\gamma_A^\infty = \frac{p\phi_A^\infty K_A^\infty}{p_A^\circ \phi_A^\circ \exp[(p - p_A^\circ)V_A/RT]} \quad (2)$$

The convention is followed that the activity coefficient of a pure liquid is unity. ϕ_A^∞ is the fugacity coefficient of component A in the elution gas mixture, ϕ_A° is the saturated vapor fugacity coefficient, V_A is the liquid molal volume, and p_A° is the vapor pressure. The saturated vapor fugacities are evaluated from second virial coefficients tabulated in Dymond and Smith (*1*) or from the generalized correlation of Lydersen, Greenkorn, and Hougen (*2*) when the second virial coefficients are not available. Fugacity coefficients of the solute vapors in the elution gas mixtures are estimated from cross virial coefficients correlated by O'Connell and Prausnitz (*3*).

Solvent was kept on the chromatograph columns through the use of a reflux presaturator and was further controlled by operation at elevated pressures as reported in Tables III–V. In all cases the mole fraction of solvent in the vapor phase was kept to less than 1%. The amount of solvent on the partition column was checked before and after each run and did not change by more than 0.5% for the data reported.

The observed K values are estimated to be accurate to 0.4%. Activity coefficients are estimated to have an uncertainty of 0.7% due to propagated uncertainties of the experimental observations. The accuracy of activity coefficients additionally depends on the accuracies of the fugacity correlations and vapor pressure and to a lesser extent also on the molal volume of the liquid. For this reason the more directly determined K values are also reported here so that the activity coefficients can be readily reevaluated with accurate values of the other quantities required in eq 1 when they are available.

The chemicals used in this work are described in Table I. Table II presents the K values and activity coefficients of infinite dilution solutes in the solvent 1-methylnaphthalene. Table III presents the solvent phenanthrene, Table IV presents 2-nonanone, and Table V presents 1-hexadecanol.

Table V. Infinite Dilution K Values and Activity Coefficients in 1-Hexadecanol

solute	K^∞	p°(solute), atm	ϕ°(solute)	Poynting term	γ^∞(solute)
		$T_{col} = 60.0$ °C, $p_{col} = 43.6$ psia			
n-hexane	0.3998	0.7537	0.9645	1.0106	1.62
benzene	0.1971	0.5151	0.9755	1.0090	1.15
		$T_{col} = 120.0$ °C, $p_{col} = 43.3$ psia			
n-hexane	1.815	3.856	0.8972	0.9961	1.55
benzene	0.9130	2.899	0.9391	1.0002	0.989
toluene	0.4338	1.296	0.9545	1.0062	1.03
ethylbenzene	0.2378	0.6337	0.9715	1.0094	1.13
p-xylene	0.2156	0.5958	0.9734	1.0095	1.09
		$T_{col} = 180.0$ °C, $p_{col} = 50.0$ psia			
n-hexane	4.280	12.54	0.7855	0.9638	1.53
benzene	2.340	9.955	0.8506	0.9791	0.954
toluene	1.315	5.015	0.8937	0.9940	1.00
ethylbenzene	0.8252	2.811	0.9256	1.0024	1.08
p-xylene	0.7348	2.597	0.9280	1.0033	1.03
n-propylbenzene	0.5234	1.654	0.9426	1.0080	1.13

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Apparent and Partial Molal Heat Capacities of Aqueous Rare Earth Nitrate Solutions at 25 °C

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Specific heats of aqueous solutions of the trinitrates of La, Pr, Nd, Sm, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu were measured from 0.1 m to saturation at 25 °C. Apparent molal heat capacities, ϕ_{cp}, were calculated for these solutions, and empirical polynomial equations were obtained which expressed ϕ_{cp} as a function of $m^{1/2}$ for each salt. The partial molal heat capacities of the solvent, $\bar{C}_{p1}$, and solute, $\bar{C}_{p2}$, were calculated from these equations. Unlike chloride and perchlorate data reported earlier, values of $\bar{C}_{p1}$ for nitrate solutions across the rare earth series did not show a two series effect. Instead, $\bar{C}_{p1}$ values at lower concentrations (0.5 and 1.0 m) appear correlated with reported first formation constants for rare earth-nitrate complexes.

Introduction

Heat capacity data for rare earth chlorides (*23*, *30*) and perchlorates (*18*) up to saturation have previously been reported. Trends across the rare earth series for heat capacity and other properties (*19*, *20*, *24–26*, *28*) for chloride and perchlorate solutions indicate a difference in the inner-sphere hydration with the lighter rare earths having a coordination number one greater than for the smaller, heavier rare earths. Any complexation in these solutions is believed to occur at higher concentrations and involve only outer-sphere interactions between cation and anion.

For rare earth nitrate solutions, the two series effect is evident (*15*, *21*, *27*, *29*) only at very low concentrations, if at all. In these solutions electrical conductance data (*7*, *22*) indicate that complex formation between the rare earth and nitrate ions is beginning to be important even at very low concentrations, with a mixture of inner- and outer-sphere complexation occurring (*1*, *2*). At low concentrations, a maximum in complex formation was found around Eu (*3*, *4*, *12*). At higher concentrations, the predominant complex is believed to be inner sphere with coordination occurring through oxygen (*1*, *8–10*, *16*). For the hydrated crystals of $Nd(NO_3)_3$ and $Pr(NO_3)_3$, three doubly bonded nitrate ions and four water molecules were found adjacent to the rare earth ion (*17*). Also at higher concentrations, electrical conductance data were interpreted to imply that the various complexing constants decrease from La to Lu (*15*).

The study reported here investigates the effect on heat capacity properties of increased cation-anion interactions for rare earth nitrate solutions relative to chloride and perchlorate solutions. The data presented are the specific heats and the apparent and partial molal heat capacities of aqueous solutions of 12 rare earth nitrates from 0.1 m to saturation at 25 °C.

Experimental Section

Apparatus and Procedure. An adiabatic single-can solution calorimeter was used to measure specific heats of solutions; a detailed description of the apparatus and procedure is given elsewhere (*18*, *23*). Basically, the value for the heat capacity of the calorimeter, plus appendages, was determined by subtraction of the heat capacity of a weighed amount of air-saturated water from the total heat capacity of the water plus calorimeter. This was done several times during the course of this work, with checks on the accuracy of the system made by using NaCl solutions at different concentrations. Average specific heats obtained in this study agreed to within 0.05% of those measured by Randall and Rossini (*13*).

Materials. Rare earth nitrate solutions at 0.1 intervals in $m^{1/2}$ ranging from 0.3 $m^{1/2}$ to near saturation were prepared from weighed portions of concentrated stock solutions and water (all weights were corrected to vacuum). The stock solutions, at concentrations near saturation, were prepared by adding an excess of rare earth oxide to reagent grade nitric acid and boiling. After filtration of the solution, the pH of the solution was lowered to the previously determined equivalence point (three anions to one cation) by adding nitric acid (see ref 19 for a more complete description). The oxides used, prepared by the Rare Earth Separation Group of Ames Laboratory, USDOE, were at least 99.85% pure by weight. The principal impurities were the adjacent rare earths, iron, and calcium, with less than 0.05% being iron and calcium. The water used was distilled from a solution of $KMnO_4$ and KOH and had a specific conductance $<1.0 \times 10^{-6}\ \Omega^{-1}\ cm^{-1}$.

The stock solutions were analyzed by EDTA titration and an oxide and/or sulfate gravimetric method, with the resulting absolute concentrations reliable to at least ±0.1% in terms of molality. Relative concentrations of a series of dilutions were at least an order of magnitude more accurate.

Saturated solutions were prepared from portions of stock solutions concentrated in a desiccator with $Mg(ClO_4)_2$. The saturated solutions were stored in contact with the rare earth nitrate crystals, formed during concentration, for at least 2 weeks at 25 ± 0.01 °C. The concentrations of the saturated solutions were determined by one or more of the previously named methods.

Results

The apparent molal heat capacity, ϕ_{cp}, for each solution was calculated from measured specific heat by using the equation

$$\phi_{cp} = \left(\frac{1000}{m} + M_2\right)s - \left(\frac{1000}{m}\right)s^{\circ} \qquad (1)$$

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