Table IV. Excess Volume of Mixing for Benzene–Mesitylene

T, °C	$x_{C_6H_6}$	V^E, cm^3 mol^{-1}
27	0.1251	−0.189
	0.2103	−0.221
	0.2461	−0.239
	0.3781	+0.026
	0.5000	+0.319
	0.6377	+0.325
	0.7518	+0.323
	0.9261	+0.163
40	0.1250	−0.078
	0.2103	+0.055
	0.2462	+0.193
	0.3781	+0.378
	0.5000	+0.448
	0.6377	+0.441
	0.7518	+0.419
	0.9261	+0.258

previously obtained for the system benzene–carbon tetrachloride are also indicated in Table II.

The change in sign of V^E for the carbon tetrachloride–mesitylene mixture can be attributed to weak complex formation. Spectroscopic evidence (*8*, *1*) indicates a 1:1 complex of carbon tetrachloride–benzene. The complex interaction increases with increasing number of methyl groups on the benzene ring and is considerably greater for the carbon tetrachloride–mesitylene mixture than the corresponding benzene system (*12*). This is to be expected since the CCl_4 is acting as an electron acceptor, and the presence of methyl groups tends to enhance the electron-donating ability of the substituted benzene. Goates et al. (*4*) suggested pi-bonding between the benzene ring and the empty 3d level of the chloride atom. This specific interaction causes a contraction in volume. An increase in the concentration of carbon tetrachloride tends to decrease complex formation (*13*). A more favorable packing arrangement or possibly enhanced unlike interaction also causes the excess volume sign change for the benzene–mesitylene mixture.

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Heats of Mixing of Tri-*n*-dodecylamine with *n*-Octane, Benzene, or Chlorobenzene

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Excess enthalpies of mixing of binary systems of tri-*n*-dodecylamine and *n*-octane, benzene, and chlorobenzene are determined at 303.15K with a solution calorimeter. In all systems the endothermic heats of mixing are not symmetric on the mole fraction scale but are nearly so on the volume fraction scale. The heats of mixing, H^E in equimolar mixtures 64.44, 1120, and 767.0 J/mol, respectively, are essentially due to the large differences in the type of molecular interactions. Exothermic contributions from possible π-bondings with the aromatic hydrocarbons are small.

Tri-*n*-dodecylamine (trilauryl) dissolved in nonpolar or slightly polar, water-immiscible organic solvents is used as the organic phase in solvent extraction processes. In the frame of a long-term program designed to provide thermochemical data by direct calorimetric measurements pertinent to the chemistry of liquid-liquid extraction processes, we now report the heat of mixing of this amine with representatives of normal aliphatic, aromatic, and substituted aromatic hydrocarbons, all commonly used as diluents in solvent extraction processes (*4*).

Experimental

Materials. The amine, a Schuchardt product, was of the highest purity commercially available and was purified by fractional distillation under reduced pressure. The fraction used gave a single peak when gas chromatographed on a 1.5-m long column of SE30 (15%) at 300°C. The estimated purity was 99.9%. The density of the purified product was $d_4{}^{25} = 0.8217$, as compared to 0.8219 given in the literature (*2*).

Benzene, analytical-grade Mallinckrodt product, and *n*-octane, analytical-grade Fluka product, were dried

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over sodium, and chlorobenzene, Eastman White Label product, over 4 Å Perlform molecular sieve for several days prior to distillation and after. The purity of the three hydrocarbons was checked by gas chromatography with a 2-m long column of Apiezon L 10% at 150°C. The purity was better than 99.85%. Densities of the solvents: benzene d_4^{30} = 0.8687, *n*-octane d_4^{25} = 0.6987, and chlorobenzene d_4^{30} = 1.0958, as compared to the literature data (*8*) of 0.8685, 0.69849, and 1.0955, respectively.

The water content of all four liquids was determined by Karl Fischer titration, and the purified compounds contained less than 0.01% of water. For all compounds one batch was used throughout this investigation.

Methods. Densities of solutions were determined with a calibrated pycnometer of ca. 16-ml capacity fitted with a capillary. The temperature was controlled at 30.00 ± 0.01°C. The experimentally determined densities (10–12 mixtures) were fitted to the function

$$d_4^{30} = A + Bx + Cx^2 \tag{1}$$

where x is the mole fraction of the amine. The values of the coefficients are given in Table I.

Calorimeter. Heats of mixing were determined at 30.000 ± 0.001°C in a Tronac Model 1000A continuous automatic titration calorimeter. The calorimeter and the general experimental procedure were described previously (*6*).

In determining the heat of mixing, 25–50 ml of the hydrocarbon or the amine or a known mixture of the two is introduced into the 50 ml-capacity reaction vessel. When thermal equilibrium is obtained, after 3 hr in a typical run, the amine or the hydrocarbon is delivered from the buret. The titrant is added continuously at a constant delivery rate up to 0.8220 ml/min. The data points are recorded in constant time intervals, usually 10 sec, and in a typical run, 42 digital readings are taken during the addition of 6 ml of titrant, the maximum capacity of the buret. Every run was repeated at least three times, the standard deviations being less than 0.01%.

Results and Discussion

The experimental results for the excess enthalpy, H^E J/mol, are listed in Table II. For each system, x_2 represents the mole fraction of the hydrocarbon solvent. The smoothed values at 0.1 mole fraction intervals, calculated from the equation

$$H^E = x_1x_2 \sum_{i=0}^{N} A_i(x_1 - x_2)^i \tag{2}$$

are compiled in Table III, along with the parameters of Equation 2 determined to fit the data by a least-squares procedure. The constants of the smoothing equation are given in the footnote along with the standard deviation

$$\sigma_d{}^H = [\Sigma(H^E{}_{\text{calc}} - H^E{}_{\text{exp}})^2/n]^{1/2} \tag{3}$$

and the maximum deviation

$$\sigma_m{}^H = |H^E{}_{\text{calc}} - H^E{}_{\text{exp}}|\text{max} \tag{4}$$

where $H^E{}_{\text{calc}} - H^E{}_{\text{exp}}$ is the difference between the values calculated from the correlating Equation 2 and the experimental value at that mole fraction.

In all three systems investigated, the H^E vs. x_1 plots are asymmetric with the maximum occurring toward low amine mole fraction, at $x_1 \sim 0.3$. This is, of course, a common phenomenon in binary systems with a large difference in the molar volumes of the components. It probably results (*1*) from an exothermic contribution with a maximum toward high amine concentrations, owing at least partially to the fact that tridodecylamine has a molar volume about six times larger than that of any of the hydrocarbons in question. Indeed, when the experimental heats of mixing are expressed on the volume fraction scale by use of the correlating equation

$$H^E = \Phi_1\Phi_2 \sum_{i=0}^{N} F_i(\Phi_1 - \Phi_2)^i \tag{5}$$

with the coefficients listed in Table IV, along with the smoothed values of the excess enthalpies of mixing H^E J/ml at 0.1 volume fraction intervals, it becomes evident that the position of the maxima is shifted in the direction of mixtures richer in the component of the larger molar volume.

Such displacement is also predicted by the regular solution theory whenever the predominant contribution to the total heat of mixing originates from nonspecific physi-

Table I. Coefficients for Least-Squares Fit of Density Data by Equation 1, g ml^{-1}, 30°C

	A	*B*	*C*
n-Octane	0.6949	0.30	−0.1774
Benzene	0.8687	−0.13	0.0788
Chlorobenzene	1.0958	−0.70	0.4217

Table II. Excess Enthalpies of Mixing of Tri-*n*-dodecylamine with Hydrocarbons at 303.15K (x_2 Mole Fraction of Hydrocarbon, H^E J/mol)

n-Octane		Benzene		Chlorobenzene	
x_2	H^E	x_2	H^E	x_2	H^E
0.1620	28.55	0.1500	408.0	0.1721	281.4
0.3117	46.90	0.2594	688.4	0.2936	467.9
0.3993	58.23	0.3450	902.5	0.4211	650.2
0.4862	61.88	0.4124	1007	0.5166	808.7
0.5487	68.48	0.4502	1031	0.6035	884.6
0.6117	74.13	0.6340	1298	0.6556	901.6
0.6486	75.91	0.7340	1347	0.7068	895.0
0.6801	78.21	0.7959	1311	0.7393	883.7
0.7144	79.47	0.8378	1235	0.8178	800.9
0.7637	81.18			0.8509	736.3
0.8019	77.52			0.8758	670.8
0.8320	73.83			0.8954	565.2
0.8563	70.77				

Table III. Smoothed Values of Excess Enthalpies of Mixing of Tri-*n*-dodecylamine with Hydrocarbons at 303.15K

x_2	*n*-Octane, $H^{E\,a}$	Benzene, $H^{E\,b}$	Chlorobenzene, $H^{E\,c}$
0.1	28.72	258.2	164.2
0.2	34.26	546.4	321.5
0.3	46.98	788.7	476.7
0.4	56.42	972.3	628.4
0.5	64.44	1120	767.0
0.6	72.37	1251	871.9
0.7	78.97	1342	908.5
0.8	78.56	1314	825.8
0.9	59.05	975.3	553.6

[a] $H^E = x_1x_2[257.7 - 158.1(x_1 - x_2) + 263.3(x_1 - x_2)^2 - 201.9(x_1 - x_2)^3]$. $\sigma_d = 1.20$ J mol^{-1}. $\sigma_m = 1.86$ J mol^{-1}. [b] $H^E = x_1x_2[4480 - 2704(x_1 - x_2) + 3695(x_1 - x_2)^2 - 3525(x_1 - x_2)^3]$. $\sigma_d = 12.6$ J mol^{-1}. $\sigma_m = 22.9$ J mol^{-1}. [c] $H^E = x_1x_2[3068 - 2525(x_1 - x_2) + 1436(x_1 - x_2)^2 - 280.3(x_1 - x_2)^3]$. $\sigma_d = 14.0$ J mol^{-1}. $\sigma_m = 29.4$ J mol^{-1}.

Table IV. Smoothed Values of Excess Enthalpies of Mixing of Tri-*n*-dodecylamine with Hydrocarbons at 303.15K (Φ_2 Volume Fraction of Hydrocarbon H^E J/ml)

Φ_2	*n*-Octane, H^{E^a}	Benzene, H^{E^b}	Chlorobenzene, H^{E^c}
0.1	0.124	2.564	1.543
0.2	0.190	4.552	2.809
0.3	0.235	6.022	3.651
0.4	0.273	6.967	4.025
0.5	0.303	7.347	3.965
0.6	0.314	7.110	3.553
0.7	0.292	6.218	2.888
0.8	0.228	4.675	2.057
0.9	0.124	2.549	1.103

[a] $H^E = \Phi_1\Phi_2[1.214 + 0.455(\Phi_1 - \Phi_2) + 0.257(\Phi_1 - \Phi_2)^2 - 0.714(\Phi_1 - \Phi_2)^3]$. $\sigma_d = 0.003$ J ml^{-1}. $\sigma_m = 0.007$ J ml^{-1}. [b] $H^E = \Phi_1\Phi_2[29.39 - 1.598(\Phi_1 - \Phi_2) - 1.537(\Phi_1 - \Phi_2)^2 + 2.665(\Phi_1 - \Phi_2)^3]$. $\sigma_d = 0.162$ J ml^{-1}. $\sigma_m = 0.39$ J ml^{-1}. [c] $H^E = \Phi_1\Phi_2[15.86 + 5.036(\Phi_1 - \Phi_2) - 1.817(\Phi_1 - \Phi_2)^2 - 0.310(\Phi_1 - \Phi_2)^3]$. $\sigma_d = 0.08$ J ml^{-1}. $\sigma_m = 0.115$ J ml^{-1}.

cal interactions (*3*). These reactions are usually endothermic, as are the heats of mixing in the systems under consideration.

The tridodecylamine-octane mixtures are the most ideal, the endothermic heats of mixing being of a comparable magnitude to those of two hydrocarbons, if one of them is slightly polar. The dipole moment of the amine is of the order of 0.3 debyes (*7*). The substantial difference in the H^E values between this system and those with the two aromatic hydrocarbons may be taken as fair evidence that the contribution of n–π interactions between the lone-pair electrons of the nitrogen atom and the π-electrons of the aromatic ring to the observed heats of mixing is small. That the H^E values are more endothermic than in the corresponding amine-octane system can best be explained by assuming that the energy needed for breaking the ring-ring bonds is not compensated by the energy of the interaction between the nitrogen of the amine and the π-electrons of the aromatic ring. Chlorobenzene is apparently a less associated liquid than benzene.

We are reporting (*5*) evidence to show that the strength of n–π interactions is strongly dependent on the length of the hydrocarbon chain in the tertiary amine molecule. Long aliphatic chains screen the nitrogen effectively and thus diminish its availability for interactions with π-electrons.

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Apparent Molal Volumes of Aqueous NaF, Na_2SO_4, KCl, K_2SO_4, $MgCl_2$, and $MgSO_4$ Solutions at 0° and 50°C

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The apparent molal volumes, Φ_V's, of dilute (0.002–1*m*) aqueous solutions of NaF, Na_2SO_4, KCl, K_2SO_4, $MgCl_2$, and $MgSO_4$ are determined at 0° and 50°C from precision density measurements made with a magnetic float densitometer. The infinite dilution apparent molal volumes, $\Phi_V{}^\circ$'s, are determined by using the Redlich equation, $\Phi_V = \Phi_V{}^\circ + S_V c^{1/2} + b_V c$, where S_V is the Debye-Hückel limiting law slope, and b_V is a deviation constant. At 0°C the deviations are positive for all the salts except $MgCl_2$. The temperature dependence of the b_V for all the salts is similar to other common electrolytes ($\partial b_V/\partial T$ is negative). The effect of temperature on the $\Phi_V{}^\circ$'s of all the electrolytes is similar in that $\partial^2\Phi_V{}^\circ/\partial T^2$ is negative. The ion–ion and ion–water interactions responsible for the observed behavior of the Φ_V's are briefly discussed.

Although there are reliable density and apparent molal volume data for many aqueous electrolyte solutions at 25°C (*8*), little reliable data are available at other temperatures (*14*). Recently (*11, 13*) we had need for reliable apparent molal volume data for some sea salts (NaCl, $MgCl_2$, Na_2SO_4, $MgSO_4$, NaF, KCl, K_2SO_4) at temperatures between 0° and 40°C. The present paper contains results of the densities and apparent molal volumes of some of these sea salts at 0° and 50°C from 0.002 to 1 molal.

Experimental

All the solutions were made by weight with reagent-grade (Baker Analyzed) chemicals (without further purification) and ion-exchanged water (Millipore Super Q). The concentrations of the KCl, K_2SO_4, Na_2SO_4, and $MgSO_4$ stock solutions were analyzed by heating to dryness, whereas the concentrations of the $MgCl_2$ stock solution were analyzed for Cl^- by titration with $AgNO_3$.

The magnetic float densitometer used to make the density measurements and a review of the development of the magnetic float method were described in detail elsewhere (*12*). The densitometer consists of a 110-cm^3 solution container which fits into a brass support containing a solenoid. The float (32 cm^3) is made of borosilicate glass and contains a magnet. The densitometer was calibrated with ion-exchanged water by using the densities (g/ml) tabulated by Kell (*7*). The density measurements

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