Integral Heats of Solution of Some Electrolytes and Water in Ethylenediamine at 25.00° C.

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Heats of solution of various electrolytes and water in anhydrous ethylenediamine have been measured in the concentration range 1.5 x 10^{-3} to about 1 x 10^{-2} molal. These results have been compared with those integral heats of solution in other anhydrous amine solvents such as NMF and DMF where available, and principally with those done in anhydrous liquid ammonia in the region of "infinite dilution" at −33.5° C. and 25.00° C. Salts having cations which permit the formation of ligands showed very large molar heat effects.

IN THE STUDY of the physical chemistry of solutions of electrolytes in anhydrous ethylenediamine (dielectric constant $D \cong 13.0$), the heats of solution of various electrolytes such as the iodides and nitrates of the alkali metals, mercury, and silver, and the heat of solution of water are compared with this same thermochemical property in other amine solvents where such data are available. Many determinations have been done in nitrogen bearing solvents such as those in anhydrous liquid ammonia by Kraus *et al.* (*4*), Schmidt *et al.* (*6*), and Mulder and Schmidt (*5*), at the boiling point and by Gunn (*1*) at 25° C. Recently, Held and Criss (*2*) have determined the ΔH_S for several of these same salts in both methylformamide NMF ($D = 182.4$) and dimethylformamide, DMF ($D = 36.7$). Comparison is made of the ΔH_S of these electrolytes in the various solvents and is shown in Table II.

EXPERIMENTAL

Materials. Ethylenediamine (98%) supplied by Matheson, Coleman and Bell was refluxed for some 12 hours over calcium hydride and then distilled into another distilling flask containing fresh calcium hydride under an atmosphere of dry oxygen-free nitrogen. From this second flask, the amine was distilled into a tared weight buret having a capacity of about 200 ml. The anhydrous solvent was weighed to the nearest milligram and transferred to the dry calorimeter in an atmosphere of dry nitrogen. Slow distillation produced ethylenediamine having a water content of less than 0.02% as determined by a Karl Fischer titration. Conductance measurements made on different samples of the distillate showed a specific conductance as low as 1–3 × 10^{-6} mho.

All salts used with the exception of Mercury II cyanide and the thallous compounds were of reagent grade and were not recrystallized. The thallous halides and nitrate were prepared from thallium metal and were recrystallized twice from distilled water and dried at 100° C. in a vacuum. All compounds were sealed under vacuum in fragile sample bulbs for use in the calorimeter.

The Calorimeter. The calorimeter is simple and consists of a vacuum jacketed borosilicate glass flask having a capacity of about 200 ml. total. The opening to the calorimeter is a 50/50 female joint. The thermowell, heating well, and bulb-breaking mechanism are all sealed into a 50/50 male joint making a single compact "sensing probe." Heat leakage is considerably lessened by this arrangement, being approximately of the order 10^{-4} calorie per degree per minute. The glass sample bulbs were broken directly against the bottom of the calorimeter. Stirring was accomplished by a magnetic stirrer. This stirring arrangement was efficient and ensured rapid dissolution of all samples. The speed of stirring was the same for all determinations.

A 22-point copper-constantan thermocouple with shielded leads gave optimum performance. The $\Delta t/\Delta$EMF for this thermopile was 1.134° C. per mv. A Leeds and Northrup type K-3 potentiometer was used in conjunction with a Leeds and Northrup direct current microvolt amplifier as a nullpoint indicator. The potentiometer was readable to an accuracy of <0.2 microvolt. With a stable reference junction, temperature changes as small as 2.2 × 10^{-4} °C. can be measured.

The calorimeter heating element is a 25-ohm copper wire cell inside of, and insulated from, a platinum tube sealed into a borosilicate glass tube. In the heating circuit, the current is taken as being equal to the voltage drop across a Leeds and Northrup 1-ohm standard resistor, and the voltage is determined by means of a voltage divider network connected across the heating coil consisting of 1000- and 10,000-ohm standard resistors. A separate Leeds and Northrup type K-2 potentiometer was used for these heating circuit measurements, thus eliminating the need for a switching arrangement, where the same potentiometer is used for both voltage-drop measurements in the heat-input circuit and the thermocouple circuit.

Stirring in the calorimeter was kept constant for all determinations and heat inputs by means of a Variac to ensure the same heat of stirring. Several determinations of the heat of solution of an identical sample deviated from one another by a maximum of 0.5%.

Reference Junction. The reference junction of the thermocouple was immersed in a Dewar flask identical in size to the calorimeter and filled with the same volume of water as the solution in the calorimeter itself. Both calorimeter and reference junction Dewar were submerged in a constant temperature bath holding 7.5 cubic feet of water. The temperature of the bath was kept at 25.00° C. ± 0.001° by means of an electronically controlled system with a short-term drift of ±0.0005° C. per hour. The drift in temperature using this type of reference junction was well within the readability of the type of K-3 potentiometer. One advantage of this reference junction over the usual ice junction is the fact that should the bath temperature drift slightly, the system is self-compensating, as the heat input into this bath is continuous and not abrupt. Therefore changes were insignificant compared to the lagtime of both calorimeter and reference.

Procedure. Previously weighed thin-walled sample bulbs having a volume of about 1 ml. and a stem of 5 mm. were blown from 5-mm. borosilicate glass tubing and were filled with the purified sample and evacuated at 100° C. for several hours. (Experience showed that 5 hours' evacuation at this temperature was sufficient to bring the sample to constant weight.) The bulbs were then sealed under vacuum. Samples ranged in size from 50 to 300 mg. depending upon the magnitude of the heat effect produced and the solubility of the particular electrolyte. The bulb was then attached to the crushing rod. The amount of ethylenediamine used for all determinations was about 188 grams or 3.15 moles. The 50/50 joint of the calorimeter was sealed with paraffin to prevent leakage of water into the calorimeter from the constant temperature bath. Both calorimeter and reference junction Dewar were submerged in the bath to a depth of 150 mm.

RESULTS AND DISCUSSION

With the exception of the heat of solution in this solvent, all determinations were made in the dilute region. The results are given in Table I. The concentrations are reported in moles solvent per mole sample to compare these results with those reported using anhydrous liquid ammonia, Kraus (*4*) and Schmidt and coworkers (*5, 6*). Comparison of ΔH_S of substances in anhydrous ethylenediamine at 25° C. (*4*) and in liquid ammonia at −33.46° C. are shown in Table II. Our results in ethylenediamine are good to slightly better than 1% while those in anhydrous liquid ammonia at −33.5° C. can be relied upon only to about 3% in many cases.

In general, the heats of solution in anhydrous ethylenediamine are equal to or more negative than those in liquid ammonia as is demonstrated in Table II. They are, however, more or less the same order of magnitude. Those

Table I. Integral Heats of Solution of Some Electrolytes and Water in Anhydrous Ethylenediamine

Moles Solvent/ Mole Salt	ΔH_S, Kcal./mole
MERCURY II IODIDE	
1927.0	−28.60
9720.0	−28.59
10,410.0	−28.62
POTASSIUM IODIDE	
221.1	−5.90
295.4	−5.90
510.0	−5.96
649.6	−6.10
984.3	−6.12
SODIUM BROMIDE	
448.8	−10.00
504.0	−9.70
726.0	−9.50
SODIUM IODIDE	
381.7	−14.55
537.8	−14.90
1272.0	−15.77
2078.0	−15.76
3279.0	−15.75
SODIUM NITRATE	
512.8	−3.28
524.1	−3.24
540.6	−3.27

Moles Solvent/ Mole Salt	ΔH_S, Kcal./mole
RUBIDIUM IODIDE	
998.0	−4.50
CESIUM IODIDE	
840.8	−2.47
ETHYLENEDIAMINE DIHYDROCHLORIDE	
1888.0	−19.55
3894.0	−20.30
4755.0	−20.32
7290.0	−20.30
THALLIUM I NITRATE	
1123.0	−11.53
1150.0	−11.40
1322.0	−11.40
THALLIUM I BROMIDE	
1384.0	−3.90
1625.0	−3.85
THALLIUM I CHLORIDE	
1202.0	−4.03
1945.0	−4.02

Moles Solvent/ Mole Salt	ΔH_S, Kcal./mole
WATER	
70.7	−3.75
88.9	−3.73
103.0	−3.77
118.7	−3.70
140.0	−3.75
146.0	−3.74
162.5	−3.71
MERCURY II CYANIDE	
1468.0	−16.60
1961.0	−17.30
14,950.0	−17.34
POTASSIUM NITRATE	
637.0	+0.98
763.0	+0.96
1252.4	+0.97
LITHIUM IODIDE	
992.2	−28.6
1500.0	−29.1
2597.0	−28.8
SILVER CYANIDE	
1118.6	−9.93
2152.8	−9.87

Moles Solvent/ Mole Salt	ΔH_S, Kcal./mole
LITHIUM NITRATE	
342.3	−10.25
1200.0	−10.32
1805.0	−10.35
SILVER IODIDE	
1615.0	−8.13
6540.0	−8.90
SILVER BROMIDE	
2265.0	−9.80
2308.0	−9.97
SILVER CHLORIDE	
871.0	−11.03
2522.0	−12.74
5722.0	−12.76
LEAD II NITRATE	
9861.0	−32.2
9854.0	−32.2
SILVER NITRATE	
5871.0	−25.17
5992.0	−25.00
5384.0	−25.00
5976.0	−24.90

Table II. Integral Heats of Solution of Salt and Water in Ethylenediamine

	Molar ΔH_S				
Salt	En.	NH_3(−33.5° C.) (*4, 5, 6*)	NH_3(25° C.) (*1*)	DMF(25° C.) (*2*)	NMF(25° C.) (*3*)
LiI	−28.80	−18.10	. . .	. . .	. . .
NaI	−15.70	−17.50	. . .	−13.95	−8.26
KI	−5.90	−5.90	−9.70	. . .	. . .
CsI	−2.47	. . .	−6.79	−4.21	. . .
HgI_2	−28.60	−20.10	−22.60	. . .	. . .
$AgNO_3$	−25.00	−21.40	. . .	. . .	. . .
$NaNO_3$	−3.27	−9.37	. . .	. . .	. . .
KNO_3	+0.97	+0.40	. . .	. . .	. . .
AgCl	−12.7		. . .	. . .	. . .
AgBr	−9.97	−8.90	. . .	. . .	. . .
AgI	−8.90	−7.40	. . .	. . .	. . .
NaBr	−10.00	−8.00	. . .		
$Hg(CN)_2$	−17.30	−13.20	. . .	−7.39	. . .
H_2O	−3.75	−1.78	calcd. to 25° C. detnd. at 25° C.	−3.80(2) −3.32(*4*)	

	Molar ΔH_S	
Salt	DMF(25° C.) (*8*)	NMF(25° C.) (*7*)
LiI	−19.09	−21.11
NaI	. . .	−8.25
KI	−8.04	−3.22
RbI	. . .	. . .
CsI	−4.25	+0.71

Comparison of the integral heats of solution in kilocalories of salts and water in ethylenediamine at 25° C. in the dilute region with heats of solution in other amine solvents and anhydrous liquid ammonia at −33.6° C. (Mole ratio of solvent salt is approximately the same for all solvents.) ΔH_S is given in kilocalories.

salts capable of complexing with the solvent show heat effects of the order of heats of reaction (10.0 kcal. or better). The ΔH_S of KNO_3 is negative, as it is in water and anhydrous liquid ammonia at −33.5° C. It should be pointed out that the ΔH_S for water in anhydrous ethylenediamine is of the same order of magnitude as it is in liquid NH_3 at 25° C. (*1*) and is independent of the concentration as shown in Table I.

If the concentration of both silver nitrate and lead II nitrate was greater than solvent-solute ratio of 6000 to 1, oxidation of the solvent took place, and the results were meaningless.

Unfortunately the alkali metals themselves are not soluble without reaction in this solvent, so no comparison could be made of ΔH_S for the metals in the simple amine solvents.

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Surface Thermodynamic Properties of Alcohols and Related Compounds

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Surface thermodynamic properties of a series of alcohols (C_6 to C_{18}), cellosolves, and carbitols have been derived from surface-tension measurements for various temperatures in the liquid or molten-solid states. A systematic variation of thermodynamic properties with respect to chain length and change in temperature was observed in the case of the series of alcohols and cellosolves. The carbitols showed an irregular behavior with respect to the chain length.

SURFACE thermodynamic properties of pure liquids or molten solids at various temperatures have been measured to understand the nature and behavior of their surface region. The contraction of the surface area of a liquid is a naturally occurring phenomenon whose final effect is to decrease the free surface energy. The free surface energy is a property of the liquid-surface region (5) and plays an important role in the interpretation of liquid-surface phenomena. Since the free surface energy of a unit area of a surface is dependent on surface tension, the surface tensions of a series of alcohols (C_6 to C_{18}, even carbon chain) and alkoxy ethanols (cellosolves and carbitols) were measured at various temperatures, and the relevant thermodynamic quantities were derived.

SURFACE TENSION MEASUREMENTS

Cellosolves, carbitols, and alcohols from C_6 to C_{18} carbon chain, obtained from the British Drug Houses in fairly pure state, were further subjected to purification processes for the required purity. Alcohols from C_6 to C_{12}, cellosolves, and carbitols were purified by repeated fractional distillation in a 65-cm. long fractionating column having a diameter of 2 cm. and packed with concentric borosilicate glass helices. The C_{14}, C_{16}, and C_{18} alcohols were first subjected to a triangular method of fractional recrystallization, with dry acetone as the solvent, followed by a process of acetylation and deacetylation. Later, the alcohols were fractionally distilled through the same column under vacuum. Purity was checked by vapor-phase chromatography using an Aerograph (A-350-B), and samples showing purity over +99% were used for measurements. The boiling point and density values available in the literature were compared with those measured in the present work (Table I).

Surface tensions of pure liquids were measured by the

Table I. Tabulation of Boiling Point and Density Values

Compounds	Boiling Points		Density	
	Obsd.	Lit.	Obsd.	Lit.
C_6H_{13}—OH	156° C./710 mm.	157.5° C./761 mm.[a]	0.8121/30° C.	0.81201/30° C.[a]
C_8H_{17}—OH	192.5° C./710 mm.	194.4° C./760 mm.[a]	0.8220/30° C.	0.82192/30° C.[a]
$C_{10}H_{21}$—OH	228.9° C./708 mm.	231° C./759 mm.[a]	. . .	. . .
$C_{12}H_{25}$—OH	113.5° C./20 mm.	114° C./20 mm.[a]	. . .	. . .
$C_{14}H_{29}$—OH	169.2° C./20 mm.	170° C./20 mm.[a]	. . .	. . .
$C_{16}H_{33}$—OH	130° C./1 mm.	190° C./20 mm.[a]	0.8149/55° C.	0.81521/55° C.[a]
$C_{18}H_{37}$—OH	150° C./1 mm.	217° C./17 mm.[a]	. . .	. . .
CH_3O—C_2H_4OH	. . .	. . .	0.9612/25° C.	0.96024/25° C.[b]
C_2H_5O—C_2H_4OH	. . .	. . .	0.9281/25° C.	0.92520/25° C.[b]
C_4H_9O—C_2H_4OH	. . .	. . .	0.8960/25° C.	0.89664/25° C.[b]
$CH_3(O$—$CH_2CH_2)_2$—OH	. . .	. . .	1.0160/25° C.	1.0167/25° C.[c]
$C_2H_5(O$—$CH_2CH_2)_2$—OH	. . .	. . .	0.9833/25° C.	0.9841/25° C.[c]
$C_4H_9(O$—CH_2—$CH_2)_2$—OH	. . .	. . .	0.9477/25° C.	0.9484/25° C.[c]

[a] Reference No. 6. [b] Reference No. 2. [c] Reference No. 7