Table IV. Surface Areas and Mean Pore Diameters

Catalyst no.	Surface areas, m²/g		Mean pore diameters, D, Å, based on		
	BET	CI	Vol	Surface	No.
1	144	105.0	111.6	46.2	22.3
2	39	26.2	120.9	77.1	54.6
3	119	78.7	80.6	52.5	39.5
4	134	75.2	123.9	60.9	29.5
5	164	155.6	82.7	39.1	24.1
6	149	148.5	103.9	40.8	22.3

NOMENCLATURE

D = pore diameter, Å
E = expected value
F = cumulative volume below D
f = volume density function
t = dummy variable
u = unit step function
V = volume, ml/g
Var = variance

Greek Symbols

α = parameter in Weibull distribution
β = parameter in Weibull distribution
γ = parameter in Weibull distribution
μ = parameter in log normal distribution
σ = parameter in log normal distribution

Subscripts

ai = upper limit of pore sizes in section i
bi = lower limit of pore sizes in section i
i = running index of sections
j = running index of pore diameter

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Heat of Mixing of Water and Diethylene Glycol Dimethyl Ether

WILLIAM J. WALLACE[1] and THOMAS J. VELLENGA
Muskingum College, New Concord, Ohio 43762

Calorimetric heats of mixing have been obtained for the system water–diethylene glycol dimethyl ether at temperatures near 25° over the entire range of composition. The heat of mixing exhibits an exothermic maximum of 491 cal/mol of solution and an endothermic minimum of 57 cal/mol of solution, at mole fractions of diethylene glycol dimethyl ether equal to 0.115 and 0.86, respectively.

Diethylene glycol dimethyl ether is a useful solvent for a number of ionic reagents, notably sodium borohydride (*1, 5*). It is a colorless, mobile liquid, with a useful liquid range of over 200° C to its normal boiling point of 162° C, and it is miscible in all proportions with water. Some hydrated salts form anhydrous etherates when brought in contact with the ether (*5*). Considerable deviation from ideality is observed in density and viscosity data for water solutions of diethylene glycol dimethyl ether (*7*). We here report the heat of mixing of water with this ether over the full range of compositions at temperatures near 25° C. Temperature changes of up to 10° are observed, and the starting temperature was chosen so that the midpoint of the temperature change due to mixing was at 25° C.

EXPERIMENTAL

Materials. Diethylene glycol dimethyl ether (Ansul Chemical Co., Ether E-141, Diglyme) was distilled from sodium under a nitrogen atmosphere at 162–3° C (uncorr.) and gave a negative peroxide test (*2*). Water content was less than 0.01% based on Karl Fischer electrometric titrations. Water was freshly distilled for each determination. Densities, refractive indexes, molar refractions, and viscosities of water–diethylene glycol dimethyl ether have been reported previously (*7*).

Calorimeter. The calorimeter consisted of an ordinary one-pint Dewar flask fitted with a stirrer, thermometer, and one of three inner vessels as shown in Figure 1. Choice of the inner vessel used depended on the desired final concentration. The procedure followed consisted of weighing the liquid of larger amount into the Dewar flask, and the other liquid into the inner vessel. The apparatus was assembled and the contents were warmed sufficiently to result in a temperature change during mixing which would be equally above and below 25° C. The stirrer was actuated by a reciprocating takeoff on an ordinary stirring motor. Temperature readings were made at regular intervals during each determination.

The liquids were mixed by crushing the thin-walled inner vessel against the bottom of the Dewar, or, in the case of the stoppered inner vessel, by opening the stopper and forcing the liquid out with a surge of dry air. The inner

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[1] To whom correspondence should be addressed.

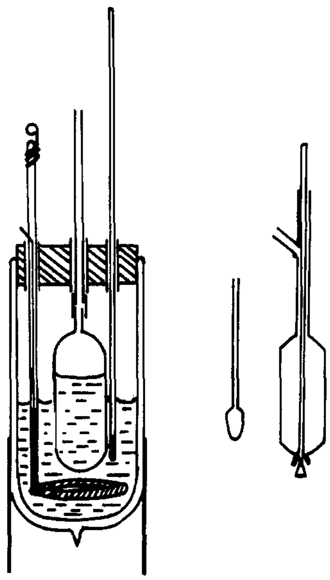

Figure 1. Calorimeter, optional inner vessels

Stirrer is wound with a manganin resistance wire heater. Stoppered inner vessel has inlet for dry airstream to push liquid out of bulb

Table I. Heat of Mixing of Diglyme and Water

Mole fraction diglyme	Molality diglyme	Molality water	Calories per mole solution	Calories per mole diglyme[a]	Calories per mole water[b]
0.0092	0.516	802.3	−64.25	−6981	−64.8
0.0174	0.982	421.4	−111.3	−6406	−113.3
0.0179	1.011	409.3	−110.0	−6154	−112.0
0.0181	1.026	403.4	−119.9	−6611	−122.1
0.0183	1.036	399.2	−115.0	−6277	−117.2
0.0360	2.074	199.4	−233.4	−6479	−242.1
0.0441	2.563	161.4	−257.5	−5833	−269.4
0.0478	2.787	148.4	−293.2	−6134	−308.0
0.0639	3.790	109.2	−337.1	−5275	−360.2
0.0823	4.975	83.14	−466.8	−5674	−508.6
0.1154	7.241	57.13	−490.7	−4252	−554.7
0.1184	7.455	55.49	−472.6	−3991	−536.1
0.2046	14.28	28.97	−414.0	−2023	−520.5
0.2743	20.98	19.72	−307.9	−1123	−424.2
0.3854	34.81	11.88	−238.3	−618.2	−387.7
0.4685	48.93	8.454	−149.0	−318.0	−280.3
0.4828	51.82	7.982	−148.9	−308.3	−287.8
0.5356	64.01	6.463	−94.43	−176.3	−203.3
0.5968	82.16	5.035	−53.65	−89.89	−133.1
0.6678	111.6	3.708	−11.64	−17.43	−35.04
0.7295	149.7	2.764	20.13	27.60	74.42
0.7770	193.4	2.139	41.23	53.06	184.9
0.8172	248.1	1.668	49.88	61.04	272.8
0.8595	339.5	1.219	57.20	66.56	407.1
0.9415	893.3	0.463	33.92	36.02	579.7
0.9521	1103.8	0.374	28.42	29.85	593.6

[a] Extrapolated heat of solution is 6.44 ± 0.37 kcal/mol diethylene glycol dimethyl ether. [b] Extrapolated heat of solution is 719 ± 17 cal/mol water.

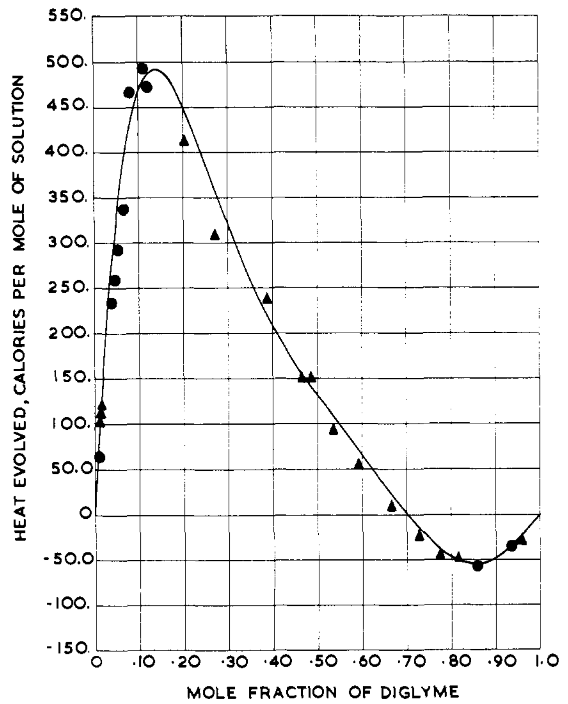

Figure 2. Heat of mixing of water and diethylene glycol dimethyl ether, calories per mole of solution

Triangles designate values obtained with stoppered inner vessel. Circles designate values obtained with breaking bulb inner vessel. The original drawing was made with a Calcomp plotter, and the smooth curve shown is a power series describing the data within 8% over the entire concentration range

vessel was raised and lowered by hand to ensure complete mixing. The heat capacity of the system was then determined as part of each measurement by passing a known electric current through a calibrated resistance wire wound about the stirrer.

The power supply for the heater was an Alpha 7500 PS unit coupled with an Alpha 7500 R current regulator (current regulated to 0.01%). Current was fed into a identical heater and switched to the calorimeter heater for an electrically timed interval. Output of the power supply was calibrated with a copper coulometer, and was reproducible to better than one part per thousand. The resistance of the heater was measured before and after each determination with a Type 1608-A General Radio Impedance Bridge. A temperature-time plot was constructed and the initial and final temperatures for the mixing and the heating operation were obtained by linear extrapolation of the heating (cooling) curves.

RESULTS AND DISCUSSION

The experimental results are shown in Table I in units of calories per mole of solution, calories per mole of ether, and calories per mole of water. The final concentration for each measurement is shown in mole fraction and molality units. Figure 2 shows these same results.

It is interesting to compare these results with those obtained by Goates and Sullivan for the dioxane-water system (*3*). Both systems exhibit minima and maxima, with the dioxane system having a 115 cal/mol of solution endothermic minimum at 0.80 mole fraction dioxane and a 140 cal/mol of solution exothermic maximum at 0.143 mole fraction dioxane compared with the present results of a 57 cal/mol of solution minimum and a 491 cal/mol maximum at respective mole fractions of diethylene glycol dimethyl ether of 0.86 and 0.115. Goates and Sullivan suggest that the 0.143 mole fraction maximum is close to a 1-to-6 stoichiometry for the dioxane-water.

Similarly, the maximum exothermic mixture in the present study is close to a 1-to-9 ratio for ether to water, corresponding in both cases to a 1-to-3 ether oxygen to water molecule ratio. Speculation on these ratios must be tempered by the recognition that viscosity data for four ether-water systems including ethylene glycol dimethyl ether and triethylene glycol dimethyl ether as well as the systems here discussed exhibit a maximum deviation in viscosity at a 1-to-2 ether oxygen-water molecule ratio (*4*, *6*, *7*, *8*). The most striking observation is in the much larger magnitude of the exothermic maximum in the present study compared to the dioxane-water system.

These results indicate strong hydrogen bonding between the ether and water. The endothermic region probably results from the breakup of the water network to form an ether-water network, with a net decrease in the number of hydrogen bonds. The strongly exothermic region probably results from ether entering the open network of water with a net increase in the number of hydrogen bonds. The maximum is larger than observed for the dioxane-water system, which may be because the open chain is able to enter the water network with less destruction of the water structure than occurs with dioxane. This is reflected by the large molal heat of solution at the low concentrations of diethylene glycol dimethyl ether in Table I.

ACKNOWLEDGMENT

Power series equations describing the variation of the heat of solution in the various concentration units were obtained using computer facilities at the Oak Ridge National Laboratory and were used to obtain the extrapolated heat of solution noted in Table I, and to plot the curve in Figure 1. This part of the work was done while the first author was a participant in the Oak Ridge Associated Universities summer research program.

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Refractive Index and Dielectric Constant of Mixtures of Carbon Tetrachloride with Benzene, *p*-Xylene, and Mesitylene

PATRICIA PEREZ, THOMAS E. BLOCK, and CHARLES M. KNOBLER[1]
Department of Chemistry, University of California, Los Angeles, Calif. 90024

Measurements at 25° C of the refractive index at seven wavelengths and the low frequency dielectric constant are reported for mixtures of carbon tetrachloride with benzene, *p*-xylene, and mesitylene. Dispersion formulas have been obtained for the refractive index, and values of the molar refraction and molar polarization are also reported.

The presence of weak complexes in liquid mixtures of carbon tetrachloride with aromatic hydrocarbons has been inferred from measurements of heats of mixing (*3*) and spectra (*1*, *9*). Recently a method has been described (*2*) by which refractive index and dielectric constant data can be used to determine the properties of such weak complexes. The present measurements are part of a study of the applicability of this method.

EXPERIMENTAL

Details of the experimental methods have been previously reported (*2*). The refractive index measurements were performed by the method of minimum deviation. The divided circle on the spectrometer could be read to 30 sec of arc so that with the 60° prism-angle cell, the refractive index could be determined with an accuracy of 2×10^{-4}. Temperatures were measured with a Beckmann thermometer that was calibrated with a standard platinum thermometer. The temperature uncertainty of ±0.03° C leads to a maximum error of 2×10^{-5} in n.

Dielectric constants were measured at 1 kHz with a General Radio 1615-A capacitance bridge. Although the accuracy of the bridge allows measurements of the dielectric constant to be made to $\pm 1 \times 10^{-5}$, the precision of the dielectric constant measurements is 0.0001. This difference is the result of variations in stray capacitance with different fillings of the cell.

Mixtures were prepared by weight (*2*), and the uncertainties in mole fraction are ±0.0001. The benzene was material purified for the previous studies (*2*). Carbon tetrachloride (Matheson, Coleman and Bell, 99.98%), mesitylene (Matheson, Coleman and Bell, 99.98%), and *p*-xylene (Phillips Petroleum, 99.95%) were dried before use by distillation from over sodium but were not purified further.

RESULTS

In Table I, we compare our refractive index data for the pure substances at three wavelengths to some literature values. For benzene and *p*-xylene, the data agree within experimental error, but for mesitylene and carbon tetrachloride there are discrepancies that lie outside the overlap of estimated errors. The refractive index measurements for the mixtures are shown in Table II. The experimental refractive indices for each mixture have been fitted by least squares to a three-term Cauchy dispersion formula

$$n = n_\infty + a/\lambda^2 + b/\lambda^4$$

where λ is the wavelength. Values of the constants n_∞, a, and b are listed in Table III. The dispersion relations fit each set of data with a standard deviation no greater than 0.0002.

Results of the dielectric constant measurements are given in Table IV. For the pure liquids the good agreement

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[1] To whom correspondence should be addressed.