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Solubility of Hexane, Phenanthrene, Chlorobenzene, and *p*-Dichlorobenzene in Aqueous Electrolyte Solutions

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The solubilities of hexane, phenanthrene, chlorobenzene, and *p*-dichlorobenzene were determined in water and in aqueous solutions of NaCl, Na₂SO₄, KCl, NaBr, and NH₄Cl at 25 °C. The salting-out effect is well represented by the Setschenow equation. A correlation based on the McDevit-Long theory is presented which gives the salting-out factor as a function of organic solute molar volume and an empirical constant characteristic of the electrolyte. The data for the chlorobenzenes suggest that the correlation may be applicable to halogenated hydrocarbons.

Introduction

A knowledge of the solubility of hydrocarbons and halogenated hydrocarbons in water and in aqueous electrolyte solutions is important in assessing the fate and effects of discharges of oil and other toxic compounds. Salt effects (salting-in and salting-out) of electrolytes have been investigated for several aromatic hydrocarbons (1-7) and theories have been proposed to explain these effects (1, 2). The effect of electrolytes on the activity coefficients of naphthalene has also been studied (8, 9). The solubilities of methane (10), butane (11), alkylbenzenes (12), medium molecular weight aromatic hydrocarbons (13), and higher molecular weight alkanes (14) in water and seawater have also been reported. Most of the experimental data fit the empirical Setschenow equation in which the logarithm of the ratio of solubility in salt solution and in water is expressed as a linear function of concentration of the electrolyte.

In this work, experimental solubilities are presented of a low molecular weight alkane (hexane), a polynuclear aromatic hydrocarbon (phenanthrene), and two halogenated aromatics (chlorobenzene and *p*-dichlorobenzene) in a number of electrolyte solutions together with a brief review of available experimental data for other hydrocarbons. The aim is to provide a fuller understanding of the extent to which electrolytes modify the properties of dilute aqueous solutions of hydrophobic compounds. These data also permit direct estimation of the effects of electrolytes on Henry's law constants, which are essential in vaporization rate calculations and on aqueous-organic partition coefficients which are frequently used as indicators of bioaccumulation.

Experimental Section

Saturated solutions were prepared by adding an excess amount of the solute in salt solutions of various concentrations for 24 h, followed by settling in a 25 °C temperature bath for at least 48 h before analysis.

The solubility of hexane in salt solutions was determined by vapor extraction followed by GC analysis using an established technique (15). The dissolved hexane was extracted by purified helium and subsequently trapped in a sample loop in liquid nitrogen. The hydrocarbon was then injected into the GC column by quick immersion of the sample loop in a hot oil bath.

The gas chromatograph was a Hewlett-Packard Model 5750 equipped with a flame ionization detector and a 10 ft. long, 1/8 in. o.d. stainless steel column packed with 10% SE 30 ultra-phase on high-performance Chromosorb P, 60/80 mesh.

The solubility of phenanthrene was determined by fluorescence, using an Aminco-Bowman spectrophotofluorometer (American Instrument Ltd.). Approximately 50 mL of aqueous salt solution saturated with phenanthrene was extracted with 5 mL of cyclohexane. No phenanthrene was detected in a second extract. Electrolyte solutions were filtered through glass wool prior to extraction. Standard calibration solutions were prepared by directly weighing 0.1 g of phenanthrene followed by serial dilution in cyclohexane to a concentration of 1 mg/L. The fluorescence intensity of the cyclohexane extract was then measured. It was often necessary to dilute the cyclohexane extract in order that the measured intensity was within the linear range of the calibration curve.

Originally, the fluorescence intensity was measured directly from the aqueous solution to determine the concentration of phenanthrene. However, it was later found that although salt solutions do not seem to interfere with the fluorescence spectra, they do have concentration quenching effects on the fluorescence intensity.

The solubilities of chlorobenzene and *p*-dichlorobenzene were determined by solvent extraction followed by GC analysis.

The *n*-hexane used was pure grade (99 mol %), chlorobenzene was of certified grade, obtained from Fisher Scientific, phenanthrene was of fluorescence grade from Eastman Kodak, and *p*-dichlorobenzene was obtained from BDH. Cyclohexane was of distilled-in-glass grade from Caledon Laboratories, Ontario. All the salts used were of reagent grade from Fisher and BDH.

Table I. Solubilities (mg/L) of Hexane, Phenanthrene, Chlorobenzene, and *p*-Dichlorobenzene in Aqueous Salt Solutions at 25 °C

salts	C_s , equiv/L	hexane	phenanthrene	chlorobenzene	<i>p</i> -dichlorobenzene
pure H ₂ O	0	12.3 ± 0.4	1.29 ^a	471.7 ± 17.8	87.15 ± 2.65
NaCl	0.31	10.48 ± 0.091			
	0.50		0.85 ± 0.025	375.97 ± 13.0	63.31 ± 3.40
	0.62	8.06 ± 0.035			
	1.00	7.54 ± 0.094	0.67 ± 0.02	287.51 ± 6.33	47.91 ± 1.33
	1.50	4.88 ± 0.059	0.48 ± 0.015	232.22 ± 6.43	37.43 ± 1.54
	2.00	3.75 ± 0.045	0.33 ± 0.011	180.25 ± 8.60	27.69 ± 0.94
	2.50	2.55 ± 0.035			
KCl	0.31	9.81 ± 0.250			
	0.50		0.89 ± 0.027		
	0.62	8.60 ± 0.240			
	1.00	6.45 ± 0.060	0.67 ± 0.020		
	1.50	5.06 ± 0.140	0.49 ± 0.015		
	2.00	3.42 ± 0.030	0.35 ± 0.011		
	2.50	4.40 ± 0.031			
NH ₄ Cl	0.31		0.99 ± 0.029		
	1.00	8.43 ± 0.110	0.83 ± 0.021		
	1.50	6.42 ± 0.045	0.66 ± 0.020		
	2.00	5.44 ± 0.043	0.51 ± 0.015		
	2.50	4.40 ± 0.031			
	0.31	10.56 ± 0.170			
	0.50		0.97 ± 0.034	398.09 ± 11.3	72.36 ± 2.74
0.62	9.91 ± 0.190				
1.00	7.93 ± 0.090	0.78 ± 0.027	342.8 ± 7.2	60.38 ± 1.18	
1.50	6.57 ± 0.060	0.61 ± 0.018	309.6 ± 2.7	48.65 ± 1.32	
2.00	5.92 ± 0.060	0.48 ± 0.014	254.33 ± 5.2	39.18 ± 2.53	
1/2 Na ₂ SO ₄	0.50		0.76 ± 0.022	333.16 ± 9.7	63.87 ± 1.92
	0.62	6.42 ± 0.060			
	1.00		0.52 ± 0.015	236.46 ± 5.9	42.42 ± 1.32
	1.24	4.19 ± 0.050			
	1.50		0.33 ± 0.010	176.93 ± 4.0	31.19 ± 1.24
	2.00	1.91 ± 0.026	0.20 ± 0.006	121.64 ± 6.7	22.95 ± 0.87

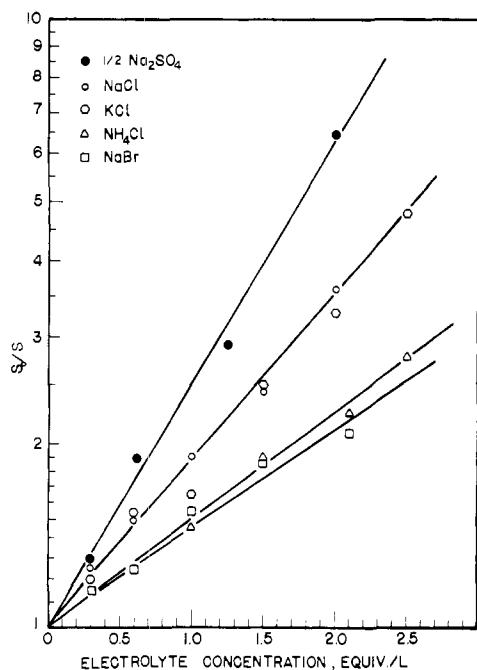
^a Reference 19.

Figure 1. Salting-out effect of various electrolytes on hexane.

Results

The solubilities of hexane, phenanthrene, and the chlorobenzenes in various concentrations of electrolyte solutions are given in Table I. The data are well correlated by the empirical Setschenow equation (1)

$$\log(\gamma/\gamma_0) = \log(S_0/S) = KC_s$$

where γ_0 and γ are the activity coefficients of the solutes in water and electrolyte solution, respectively, S_0 and S are the mole fraction solubilities of the solute in water and salt solution, respectively, K is the Setschenow constant, and C_s is the molar

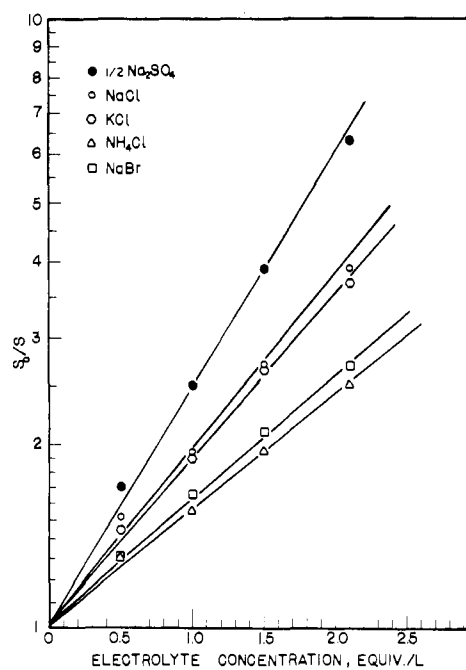


Figure 2. Salting-out effect of various electrolytes on phenanthrene.

concentration (g-mol/L) of the salt solution. Plots of $\log(S_0/S)$ vs. C_s for the four solutes are given in Figures 1–3. A least-squares straight line fit of these solubility data gives the slope and hence the constant K . The value of this constant depends upon the electrolyte and hydrocarbon. When the solubility is low (as applies here), the Setschenow constant K may be equated to the theoretical salt parameter k_s (2). Values of k_s obtained here and previously (1–8) are summarized in Table II.

From Figures 1–3, it is evident that the salting-out effect of the electrolyte decreases for anions in the order $SO_4^{2-} > Cl^-$

Table II. Experimental and Literature Setschenow Constants at 25 °C

	benzene	toluene	naphthalene	biphenyl	phenanthrene	methylcyclopentane	pentane	hexane	chlorobenzene	p-dichlorobenzene
molar vol, V_H , cm^3/mol	88.7	106	125	149	181.9	112.4	115.2	130.6	101.8	117.8
NH_4Cl	0.103 ^a	0.055 ^b			0.195			0.181		
NaBr	0.155 ^a		0.169 ^c	0.209 ^c	0.211			0.161	0.1292	0.1744
KCl	0.166 ^a	0.205 ^b	0.204 ^c	0.255 ^c	0.279			0.244		
	0.195 ^a	0.267 ^b								
NaCl	0.185 ^d	0.1953 ^d	0.260 ^c	0.276 ^c	0.287	0.273 ^d	0.221 ^d	0.276	0.2090	0.2448
	0.184 ^e	0.2052 ^e								
$1/2\text{Na}_2\text{SO}_4$	0.274 ^a	0.217 ^b	0.358 ^c	0.423 ^c	0.392			0.394	0.2904	0.2925

^a Reference 1. ^b Reference 5. ^c Reference 4. ^d Reference 6. ^e Reference 7.

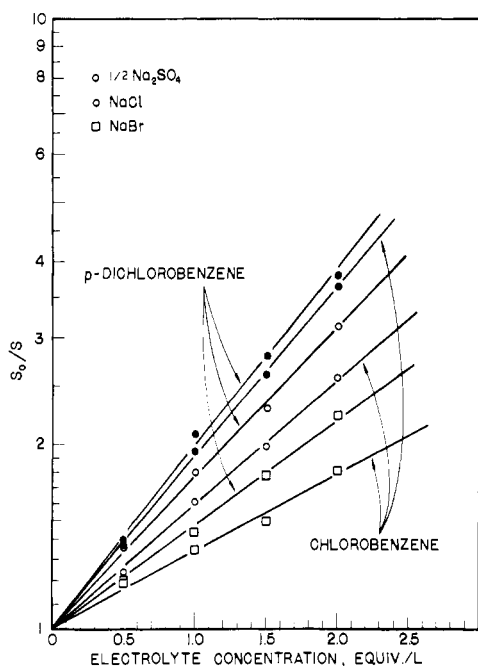


Figure 3. Salting-out effect of various electrolytes on chlorobenzene and p-dichlorobenzene.

> Br^- and for cations the order of $\text{K}^+ > \text{Na}^+ > \text{NH}_4^+$. The results, except for K^+ , are consistent with the solubilities of benzene in salt solutions reported by McDevit and Long (1) and others (3-5). From Figure 2, the order of salting-out effect of phenanthrene is consistent with the previous work.

Discussion

The tabulated values of the salting-out constants in Table II are generally in good agreement with the values presented by McDevit and Long. They have suggested that k_s can be given by the expression

$$k_s = \frac{V_H(V_S - V_0)}{2.303\beta RT} = V_H\phi$$

where V_H is the partial molar volume of the hydrocarbon in solution, V_S is the molar volume of the liquid salt, V_0 is the partial molar volume of the salt in solution all at the system temperature (T), and β is the compressibility of pure water. Unfortunately, there is often a considerable discrepancy between calculated and observed values of k_s which is probably attributable to uncertainties in the true values of the molar volumes. The only easily experimentally accessible property of the hydrocarbon is the molar volume of the pure liquid hydrocarbon which differs from V_H by some unknown amount. There is thus little alternative to using V_H in the equation. The other terms are functions of the properties of water and of the salt and can be lumped together in a single constant ϕ in the equation above.

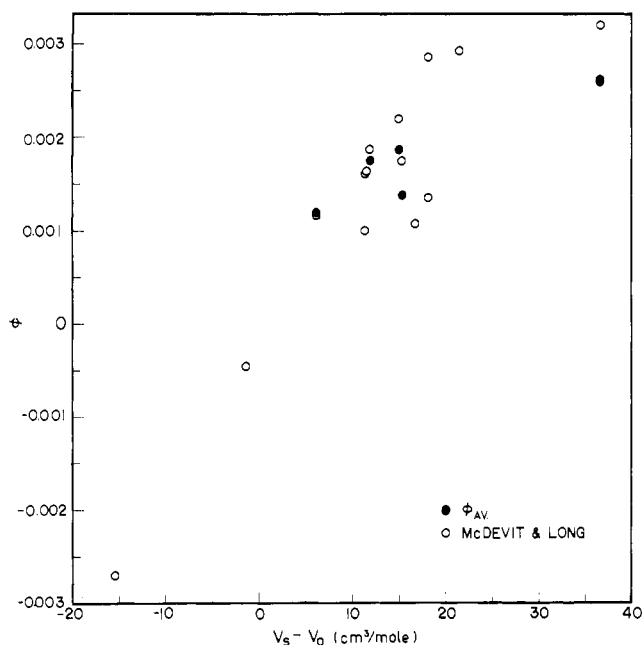


Figure 4. Empirical constant ϕ as a function of $(V_S - V_0)$.

The calculated values of this constant for various hydrocarbons and electrolyte solutions are summarized in Table III. The data show consistency in that the value of ϕ for one salt is relatively constant for the hydrocarbons studied, which range in molar volumes from 88 to 182 cm^3/mol . Values of ϕ are, however, only in poor agreement with the values calculated from the McDevit-Long theory (1) and literature values of V_0 and V_S from Millero (16, 17).

Interestingly, the chlorinated aromatics show similar ϕ values to the hydrocarbons suggesting that these compounds can be included in the same correlation procedure. This is useful since many of these compounds are of environmental concern and estimates of their aqueous phase behavior are frequently required. This similarity in behavior is thus very convenient and is to be expected since both classes have similar hydrophobic properties.

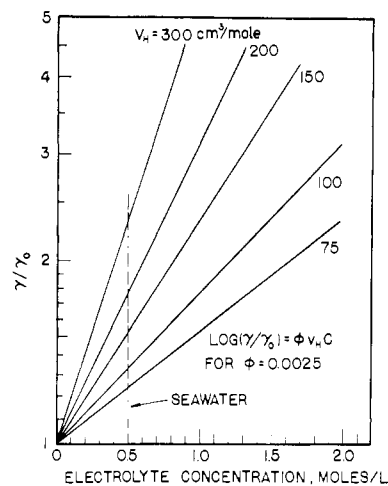
It would be desirable to relate ϕ to the properties of the electrolyte since this would permit the extent of salting-out to be predicted for other electrolytes. This is attempted in Figure 4, which is a plot of ϕ as a function of $(V_S - V_0)$. Some degree of correlation is apparent but the scatter is too large to permit accurate values of ϕ to be estimated from salt molar volume data. There is little doubt that this approach is valid in principle since, as has been demonstrated by McDevit and Long (1), compounds such as HClO_4 and $(\text{CH}_3)_4\text{NBr}$ which have negative values of $(V_S - V_0)$ exhibit salting-in behavior. The equation's failure to predict ϕ or k_s accurately is probably a result of differences between the partial and liquid molar volume of the hydrocarbon and on complex influences of the electrolytes on

Table III. Experimental and Literature Values of ϕ at 25 °C

molar vol, V_H , cm^3/mol	benzene		toluene	naphthalene	biphenyl	phenanthrene	phenanthrene	phenanthrene	methylcyclo- pentane	pentane	hexane	chlorobenzene	<i>p</i> -dichloro- benzene	average	$V_S - V_0$, cm^3/mol
	88.7	0.00116	106	125	149	181.9	181.9	112.4	115.2	130.6	101.8	117.8	117.8	average	
NH_4Cl		(0.000519)				0.00107								0.00120	6.12
NaBr	0.00175		0.00135	0.00140	0.00140	0.00116				0.00123	0.00118	0.00148	0.00136	0.00136	15.22
KCl	0.00187	0.00194	0.00163	0.00171	0.00153	0.00153				0.00187		0.00208	0.00176	0.00176	11.85
NaCl	0.00124	0.00189	0.00208	0.00185	0.00158	0.00158	0.00198		0.00192	0.00211	0.00202	0.00248	0.00187	0.00187	14.98
$1/2 \text{Na}_2\text{SO}_4$	0.00309	0.00205	0.00286	0.00284	0.00217	0.00217				0.00302	0.00284	0.00248	0.00266	0.00266	36.68

Table IV. Setschenow Constants and ϕ Values for Seawater at 25 °C

molar vol, cm^3/mol	exptl value	calcd value	ϕ	naphthalene	biphenyl	phenanthrene	dodecane	tetradecane	hexadecane	octadecane	eicosane	hexacane	average
				125	149	181.9	228.7	259.3	292.1	327.6	358.3	456.5	average
	0.3031 ^a	0.4119 ^a		0.3871 ^b	0.22 ^b	0.25 ^b	0.68 ^b	0.95 ^b	0.68 ^b	0.373 ^b	0.00190	0.00488	0.00236
	0.2531 ^c	0.1778 ^a	0.1922 ^a	0.00213	0.260 ^b	0.298 ^b	0.336 ^b	0.000964	0.00233	0.00290	0.00190	0.00488	0.00236
	0.1504 ^a	0.00276	0.00242	0.00213	0.000962	0.000964	0.00233	0.000964	0.00233	0.00290	0.00190	0.00488	0.00236

^a Reference 13.^b Reference 14.^c Reference 9.Figure 5. Illustration of the effect of various sea salt ($\phi = 0.0025$) concentrations on the ratio of activity coefficient in electrolyte solution to activity coefficient in water for organic solutes of various molar volumes.

the water structure. Ultimately a satisfactory quantitative expression for k_s may be obtained but for immediate practical purposes it is suggested that the behavior of various organic solutes in an electrolyte solution can best be correlated using the empirically determined ϕ . Where no value for ϕ is available, an approximate value can be estimated from Figure 4 from the salt's ($V_S - V_0$) value. For electrolyte mixtures the best approach may be to calculate ϕ for the mixture by weighting the component ϕ 's in proportion to their mole fractions. This is essentially the method proposed by Gordon and Thorne (8, 9). For organic solute mixtures it is unlikely that there is significant interaction between solutes; thus each can be assumed to behave independently.

Seawater is a particularly important and interesting electrolyte solution. Data for seawater are reviewed in Table IV and a mean value of ϕ of about 0.0025 is obtained.

To assist rapid and easily comprehensible estimation of the effect of electrolytes on solute properties, it is suggested that a graph such as Figure 5 provides a useful presentation of the data. This figure illustrates the effect of seawater ($\phi = 0.00236$) at various concentrations on the activity coefficient of various solutes with the stated molar volumes. Since aqueous solubility is inversely proportional to activity coefficient for sparingly soluble solutes, the ordinate gives the factor by which the solubility decreases. For Henry's law constant between air and water and for the organic-water phase partition coefficient, the ordinate gives the factor by which the quantity increases. Most environmental waters have salt concentrations varying from 0 to 0.5 mol/L (the approximate concentration of seawater (18)). Thus the factor by which these properties change is seen to range from 1.2 to 2.3 for solutes of molar volume 75 and 200 cm^3/mol , respectively, at seawater concentrations. The effect is sufficiently large to warrant quantifying for situations in which these solutes may experience saline conditions. For fresh water systems, the effect of electrolytes on the solute's environmental properties is probably less than the environmental effect of the electrolyte itself.

Conclusion

Data have been presented in the form of Setschenow constants for the salting-out properties of hexane, phenanthrene, and two chlorobenzenes in various electrolytes, which are consistent with previous data. An examination of these and other data indicates that the McDevit-Long theory provides an adequate description of the behavior of different organic solutes for a given electrolyte by using the solute liquid molar volume.

The theory is only qualitatively correct in predicting the behavior of different electrolytes and it is suggested that for practical purposes an empirical constant ϕ characteristic of the electrolyte be used. Values of ϕ are given for various electrolytes and for seawater, which permit the rapid calculation of the effect of the electrolytes in salting-out or decreasing the aqueous solubility of organic solutes or increasing their Henry's law constants or organic-water partition coefficients. The data for the chlorobenzenes suggest that properties of halogenated hydrocarbons, which are of considerable environmental concern, may be calculated using existing data for hydrocarbons.

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Heat Capacities of Some Binary Aromatic Hydrocarbon Mixtures Containing Benzene or Toluene

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A Picker flow microcalorimeter was used to determine volumetric heat capacities at 298.15 K for mixtures of benzene with toluene and for the eight binary systems formed by mixing these components separately with ethylbenzene and the three isomeric xylenes. Excess heat capacities obtained from the results are compared with the temperature variation of excess enthalpies from the literature.

Previous studies in our laboratory have demonstrated the suitability of the Picker flow calorimeter for determining differences of the volumetric heat capacities of organic liquids and their mixtures (4, 6). The present paper describes the results of applying this technique to obtain the excess heat capacities of binary systems formed by mixing benzene with toluene, ethylbenzene, *o*-xylene, *m*-xylene, and *p*-xylene and by mixing toluene with ethylbenzene, *o*-xylene, *m*-xylene, and *p*-xylene. Direct determinations of the excess heat capacities of these mixtures have not been reported previously, although there have been many investigations of their excess enthalpies (1, 2, 8-12, 14-16, 18).

Experimental Section

The component liquids were reagent grade solvents which were purified by GLC. Densities ρ and refractive indices n_D characterizing the samples used for the calorimetric studies are as follows: benzene 0.873 69 and 1.497 90, toluene 0.862 25 and 1.494 06, ethylbenzene 0.862 62 and 1.493 19, *o*-xylene 0.875 85 and 1.502 82, *m*-xylene 0.859 86 and 1.494 56, and *p*-xylene 0.856 74 and 1.493 11. In most cases these are averages of determinations for several different preparations during the course of the investigation. For individual samples,

the variations of the results from these averages were less than $\pm 0.000\ 05\ \text{g cm}^{-3}$ and $\pm 0.000\ 03$ for the densities and refractive indices, respectively. The characteristics given above are very similar to those of the component liquids we have used in other recent studies (5, 7, 17) and are in reasonable agreement with the literature values (13).

Mixtures were prepared by mass as in our earlier work (4). The error of the mole fraction is estimated to be less than 5×10^{-5} . Differences of volumetric heat capacity $\Delta(C_p/V)$ were determined in a Picker flow calorimeter, following the operating techniques described previously (4, 6). A temperature increment of 1.4 K centered on 298.15 K was used for all measurements. Each system was studied by a stepwise procedure with a mole fraction difference of about 0.1 between the test and reference liquids. Benzene and toluene were used as initial reference liquids for the two series of systems. A value of $135.760\ \text{J K}^{-1}\ \text{mol}^{-1}$, derived from our previous work (6), was adopted for the heat capacity of benzene at 298.15 K; the heat capacity of toluene was obtained from the present measurements on benzene-toluene mixtures. Corrections were applied for power losses, and in order to cancel mixing effects (6), all measurements were repeated with the test and reference liquids interchanged. The precision of the excess heat capacities is believed to be about $\pm 0.02\ \text{J K}^{-1}\ \text{mol}^{-1}$.

Results and Discussion

The experimental measurements are summarized in Table I. At any mole fraction, $\Delta(C_p/V)$ is the amount by which the volumetric heat capacity of the mixture exceeds that of the preceding mixture. As indicated above, each entry for $\Delta(C_p/V)$ is an average of measurements taken with the roles of the two mixtures reversed (i.e., as test and reference). Molar heat capacities were obtained from the volumetric heat capacities using molar volumes calculated from the densities of the component liquids and the excess volumes of the mixtures (10, 14, 17).

[†] National Research Council of Canada Research Associate 1975.