aqueous weight ratio of 1:1 as a function of N_{AC}. Substantially less is needed for the carboxylate at zero and at two alkyl carbons and a little less for N_{AC} = 3 or 4.

In summary, the results presented here indicate no major differences between the miscibility of aqueous-hydrocarbon systems containing alkylbenzenesulfonates and alkylbenzenecarboxylates, under otherwise comparable conditions. At low degrees of alkyl substitution, carboxylates appear somewhat more effective in attaining miscibility than sulfonates.

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Excess Volumes of Mixing of Binary Mixtures of Arsenic Tribromide with Benzene, Cyclohexane, and Carbon Tetrachloride at 303.15, 308.15, and 313.15 K

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Excess volumes, V^E, of binary mixtures of arsenic tribromide with benzene, cyclohexane, and carbon tetrachloride have been calculated from experimental density data at 303.15, 308.15, and 313.15 K over the entire composition range. The V^E for solutions of arsenic tribromide with benzene are negative indicating the strong intermolecular interactions between the components resulting in the formation of a 1:1 charge-transfer type complex. For the other two binary mixtures V^E is positive. V^E decreases with an increase of temperature for the binary mixtures studied.

Introduction

In this laboratory, we have been interested in the determination of thermochemical and thermodynamic properties of halides and their solutions with organic solvents (*1*). As a part of our investigation, excess volumes of mixing for the binary mixtures of arsenic tribromide with benzene, cyclohexane, and carbon tetrachloride have been determined at 303.15, 308.15, and 313.15 K over the entire composition range and reported in this paper.

Experimental Section

Preparation of Arsenic Tribromide. Arsenic tribromide was synthesized by refluxing a slight excess of the arsenic metal (A.R. Grade) with bromine in carbon tetrachloride solution till the solution was no longer brown. The solution was filtered hot, the solvent was distilled off, and the compound was finally distilled over the metal under vacuum.

Purification of Solvents. The organic solvents, viz., benzene, cyclohexane, and carbon tetrachloride were purified according to standard procedures (*2*). Some measured physical properties of these liquids have been compared with the literature values (*2–4*) in Table I.

Density Measurements. The excess volumes of mixing have been calculated from experimental density data. We preferred this method for estimation of V^E over the direct dilatometric measurements because of the chemically agressive nature of arsenic tribromide toward the blocking fluid mercury.

A single stem capillary pycnometer of ~20-cm^3 capacity was used for all our measurements. The stem consisted of a 1 mm i.d. precision bore capillary, having a reference mark lightly etched all around. The pycnometer was filled with a hypodermic syringe fitted with a specially long needle, care being taken to avoid trapping of fine air bubbles. Corrections for buoyancy and vapor space were applied. The temperature equilibrium was achieved by keeping the pycnometer in a thermostat controlled to ±0.01 °C for 6–8 h. The temperature fluctuations were observed with a 5° Beckmann thermometer graduated in 0.01 °C and absolute temperature was measured by calibrated thermometer to ±0.05 °C. The liquid meniscus in the capillary stem was read by a traveling microscope to ±0.01 mm.

The solutions for the measurement of density were prepared by weight in well-stoppered Pyrex glass bottles. The bromide being less volatile was weighed first. After the addition of organic solvent the contents of the stoppered bottles were thoroughly mixed. The use of male joints on the mixing bottles minimized the possibility of wetting glass joints which were used ungreased. Precautions were taken to reduce vapor losses during the preparation of the solutions and their transfer to the pycnometers. Corrections to the composition changes resulting from vapor losses were made whenever unavoidable losses occurred. Internal checks on the validity of these corrections to the composition were made by preparing a number of solutions in situ in a single-stem pycnometer. Duplicate densities agreed within 2×10^{-5} g cm^{-3}. The maximum uncertainty in excess volumes is expected to be around 0.005 cm^3 mol^{-1}.

Results and Discussion

The excess volumes of mixing V^E for the binary mixtures at 303.15, 308.15, and 313.15 K are recorded in Table II and are

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Table I. Some Physical Properties of the Liquids Used[a]

liquid	freezing, temp, K	refractive index at 313.15 K	density, g/cm^3 303.15 K	density, g/cm^3 308.15 K	density, g/cm^3 313.15 K
$AsBr_3$	304.05	1.6875	3.374 54[b]	3.362 02	3.349 49
	(304.15)		(3.383 2)[c]	(3.369 2)[c]	(3.355 5)[c]
C_6H_6	278.75	1.4888	0.868 18	0.862 25	0.857 31
	(278.68)	(1.4882)[b]	(0.868 36)	(0.862 7)	(0.857 69)
c-C_6H_{12}	279.80	1.4149	0.768 23	0.764 09	0.760 08
	(279.70)	(1.4154)	(0.769 14)	(0.764 38)[b]	(0.759 62)[b]
CCl_4		1.4475	1.574 80	1.565 35	1.555 71
		(1.4481)[b]	(1.574 8)	(1.565 25)[b]	(1.555 7)

[a] Values in parentheses show the literature values (*2–4*). [b] Extrapolated value. [c] From liquid density equation (*4*).

Table II. Excess Volumes of Mixing, V^E (cm^3 mol^{-1}), for the Binary Mixtures

X_1	V^E at 303.15 K	V^E at 308.15 K	V^E at 313.15 K
Benzene (1) + Arsenic Tribromide (2)			
0.0654	−0.075		
0.0918	−0.135	−0.199	−0.232
0.1192	−0.179		
0.2102	−0.374	−0.405	−0.513
0.3636	−0.597		−0.701
0.3678		−0.629	
0.5076	−0.636	−0.692	−0.716
0.6634		−0.636	
0.7896			−0.508
0.8079	−0.347	−0.441	
0.8498			−0.424
0.8919		−0.255	−0.345
0.9298	−0.157	−0.174	−0.252
0.9521	−0.107		
0.9786		−0.048	−0.096
Cyclohexane (1) + Arsenic Tribromide (2)			
0.0940	0.110		0.065
0.0969		0.082	
0.1746			0.117
0.2220	0.246	0.200	0.145
0.3147		0.263	0.208
0.4573	0.374	0.310	0.270
0.4988			0.272
0.5494		0.308	
0.5693	0.390		
0.6029			0.252
0.6149	0.380		
0.7201	0.342	0.237	0.192
0.8892	0.198	0.126	0.074
0.9599	0.085		
0.9692	0.057	0.038	0.021
Carbon Tetrachloride (1) + Arsenic Tribromide (2)			
0.0977	0.031	0.012	
0.1972	0.067	0.039	0.023
0.2918	0.090	0.072	
0.3214	0.095		0.045
0.3905	0.116	0.098	0.068
0.4858	0.154		0.098
0.5882	0.170	0.156	
0.6930	0.181	0.175	0.147
0.7880	0.160	0.150	0.112
0.8899	0.099	0.081	0.058
0.9139	0.080	0.060	

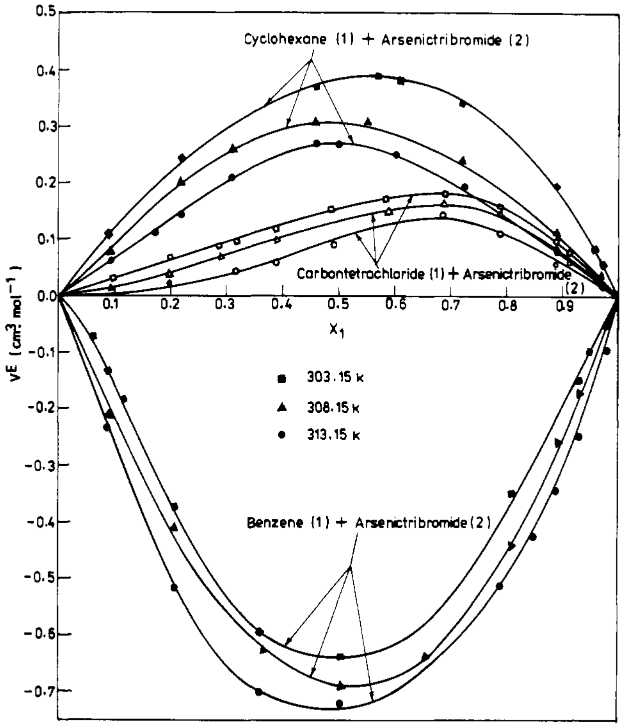

Figure 1. Excess volumes, V^E, as a function of composition for binary mixtures at various temperatures.

Table III. Parameters of Equation 1 and Standard Deviation $\sigma(V^E)$ of Experimental Values

system (1) + (2)	temp, K	parameters of eq 1 A	parameters of eq 1 B	parameters of eq 1 C	stand dev $\sigma(V^E)$, cm^3 mol^{-1}
C_6H_6 + $AsBr_3$	303.15	−2.620	−0.219	1.073	0.006
	308.15	−2.789	−0.270	0.439	0.002
	313.15	−2.920	−0.160	−0.605	0.004
c-C_6H_{12} + $AsBr_3$	303.15	1.526	0.357	0.228	0.002
	308.15	1.244	0.062	−0.207	0.003
	313.15	1.074	0.028	−0.585	0.002
CCl_4 + $AsBr_3$	303.15	0.615	0.476	0.138	0.005
	308.15	0.575	0.520	−0.100	0.003
	313.15	0.427	0.504	−0.119	0.004

plotted as a function of composition in Figure 1. The excess volumes are expressed by the equation

$$(V^E/X_1X_2) = A + B(X_1 - X_2) + C(X_1 - X_2)^2 \qquad (1)$$

where A, B, and C are disposable parameters and X_1 and X_2 are the mole fractions of components 1 and 2, respectively, in the mixtures. The parameters A, B, and C evaluated by least-squares methods are recorded in Table III along with standard deviation σ (V^E).

It is observed that the mixtures composed of arsenic tribromide and benzene show a contraction on mixing with a minimum at equimolar concentration (Figure 1) which can be attributed to the strong intermolecular interactions between the two components resulting in the formation of a 1:1 charge-transfer type complex (*5*). The excess volumes for mixtures of arsenic tribromide with cyclohexane and with carbon tetrachloride are positive at all three temperatures over the entire composition range. The plot of V^E as a function of composition for mixtures containing carbon tetrachloride is skewed toward the carbon tetrachloride end showing a maximum at $X_{AsBr_3} \simeq 0.3$. It has been observed that V^E decreases with an increase of temperature for the three binary mixtures studied.

To the best of our knowledge no other V^E data have been reported in literature for the binary mixtures considered here to compare our results.

Further thermodynamic investigations on these binary mixtures are under way.

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Vapor–Liquid Equilibrium in Methane + Quinoline Mixtures at Elevated Temperatures and Pressures

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Compositions of coexisting vapor and liquid phases at equilibrium were experimentally determined for mixtures of methane + quinoline in a flow apparatus at 189.6, 269.7, 349.5 and 429.7 °C. Measurements were made at seven pressures from 20 to 250 atm at each of the three lower temperatures and from 30 to 220 atm at the highest temperature.

Introduction

Gas–liquid equilibrium data of mixtures of methane and heavy solvents are of industrial and technological interest. Correlations of methane solubility and solvent volatility are depended upon for engineering design and analysis, and experimental data are needed for developing and checking correlations.

In this work we determine the compositions of coexisting equilibrium vapor and liquid phases of mixtures of methane + quinoline at elevated temperatures and pressures. No previous investigations of this mixture system have been reported in the literature. Sebastian et al. (*2*) reported the vapor pressure of quinoline and vapor–liquid equilibrium in mixtures of hydrogen + quinoline.

Experimental Section

The experimental apparatus and procedure of this study have been described (*3*). Attainment of equilibrium in the flow apparatus used has been examined with care in some of our previous reports (*1*, *3–5*).

As a result of experience gained in the operation of the apparatus, we have improved the control of temperature. Fluctuations of temperature of the equilibrium cell in the course of measurement of all the points on an isotherm were reduced to within 0.17 °C at the highest temperature and within 0.11 °C at the other three temperatures. The temperature of the preheated stream was controlled to within 0.5 °C of the equilibrium cell temperature.

Methane gas was supplied by Matheson with a purity of 99+%. Quinoline purchased from Fisher Scientific Co. is certified reagent grade of 99+% purity but showed a deep purple color. The color was removed and purity improved by vacuum fractional distillation over zinc as described by Sebastian and co-workers (*2*).

Table I. Vapor–Liquid Equilibrium Data for Mixtures of Methane + Quinoline

p, atm	x_M	y_M	K_M	K_Q
		189.6 °C		
19.91	0.0197	0.9815	49.82	0.0188
29.98	0.0296	0.9865	33.34	0.0139
49.9	0.0488	0.9901	20.28	0.0104
100.2	0.0945	0.9919	10.49	0.0089
149.4	0.1352	0.9919	7.33	0.0094
200.0	0.1750	0.9904	5.66	0.0117
249.7	0.2112	0.9888	4.68	0.0143
		269.7 °C		
19.90	0.0206	0.8876	43.09	0.1148
29.91	0.0311	0.9187	29.53	0.0839
50.0	0.0529	0.9449	17.86	0.0582
99.3	0.1036	0.9612	9.28	0.0433
152.4	0.1571	0.9643	6.14	0.0424
199.4	0.2025	0.9633	4.75	0.0460
249.1	0.2455	0.9622	3.92	0.0501
		349.5 °C		
19.83	0.0170	0.5838	34.34	0.4234
30.11	0.0304	0.7052	23.21	0.3040
49.8	0.0557	0.7999	14.35	0.2119
99.9	0.1191	0.8692	7.30	0.1485
151.3	0.1831	0.8866	4.84	0.1388
199.5	0.2410	0.8886	3.69	0.1468
249.0	0.3010	0.8837	2.94	0.1664
		429.7 °C		
30.03	0.0170	0.2716	15.98	0.7410
50.4	0.0514	0.4770	9.28	0.5514
99.9	0.1379	0.6381	4.63	0.4198
152.0	0.2283	0.6802	2.98	0.4144
175.2	0.2767	0.6752	2.44	0.4490
200.2	0.3311	0.6639	2.01	0.5025
220.2	0.4027	0.6391	1.59	0.6043

Samples were collected from the condensates of both the overhead and bottom cell effluents for all experiments and analyzed by gas chromatography. No significant products from decomposition were detected at any of the conditions studied.

Results and Discussion

The observed coexisting equilibrium phase compositions are reported in Table I. At the three lower temperatures, data were taken in the pressure range of 20–250 atm. The pressure range

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