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Molar Excess Volumes and Molar Excess Enthalpies of Aromatic Hydrocarbons (A) + *o*-Chlorotoluene (B) Mixtures at 298.15 K

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Molar excess volumes, V^E, and molar excess enthalpies, H^E, have been determined at 298.15 K by using a dilatometer and an LKB flow microcalorimeter, respectively, for benzene (A), toluene (A), *o*-xylene (A), *m*-xylene (A), or *p*-xylene (A) + *o*-chlorotoluene (B) mixtures. While both the V^E and the H^E values are positive for benzene (A) + *o*-chlorotoluene (B) mixtures, they are negative for the rest of the binary mixtures. The data have also been compared with the available literature values.

Introduction

Recent years have witnessed considerable interest (*1-7*) in the thermodynamic excess properties of halobenzene (A) + aromatic hydrocarbons (B) mixtures. However, considerable disagreement exists between the H^E data reported in the literature (*7*) for the toluene (A) + *o*-chlorotoluene (B) mixture. It would, therefore, be worthwhile to redetermine molar excess volumes, V^E, and molar excess enthalpies, H^E, for benzene (A), toluene (A), *o*-xylene (A), *m*-xylene (A), or *p*-xylene (A) + *o*-chlorotoluene (B) mixtures.

Purification of Materials

Analytical grade benzene, toluene, *o*-xylene, *p*-xylene, *m*-xylene, and *o*-chlorotoluene were purified as suggested in the literature (*8*). The purity of the final compounds was checked by measuring their densities at (298.15 ± 0.01) K. These agreed to within ±0.000 05 g cm^{-3} with the values reported in the literature (*9-12*) as is evident from Table I; for *o*-chlorotoluene the density at 298.15 K was evaluated from the density data reported at different temperatures in the literature (*7*).

Experimental Section

Molar excess volumes, V^E, at 298.15 K for the various binary mixtures were measured in a three-limbed specially designed dilatometer (*13*) in the manner described elsewhere (*13*).

Molar excess enthalpies, H^E, at 298.15 K were measured by an LKB flow microcalorimeter (LKB-2107, LKB Broma, Sweden) in the manner described by Monk and Wadso (*14*). According to the specification of the instrument, the temperature can be set with a precision of 0.1 K and its stability is ±0.02 K/24 h. Two identical Braun perfusor pumps (B. Braun, Melsungen AG, W. Germany) and gas-tight Hamiltom syringes were employed to pump liquids through the calorimeter. By use of 10-, 20-, and 50-cm^3 syringes and the 10-speed gear boxes of the perfusor pumps, different mixing ratios were achieved. The flow rates were determined by pumping distilled water through the calorimeter and weighing the amounts collected in a specific time interval. For each typical H^E measurement, different calibration constants were determined according to the flow rate, the amplification needed, and the composition of the mixture. The performance of the calorimeter was checked (*15*) by measuring H^E values for benzene (A) + carbon tetrachloride (B) mixtures at 298.15 K and these agreed to within the experimental limits with the corresponding literature values (*16*).

Table I. Comparison of the Measured Densities at 298.15 ± 0.01 K of the Various Compounds with Their Corresponding Literature Values

compound	density, g mL^{-1} this work	density, g mL^{-1} lit.	ref
benzene	0.873 68	0.873 63	Nyvlt et al. (*9*)
toluene	0.862 26	0.862 32	Kyle et al. (*10*)
o-xylene	0.876 00	0.875 96	Forziati et al. (*11*)
m-xylene	0.859 85	0.859 90	Forziati et al. (*11*)
p-xylene	0.856 73	0.856 69	Forziati et al. (*11*)
o-chlorotoluene	1.076 44	1.076 40	Timmermans (*12*)

Results

Molar excess properties X^E (X = V or H) for the various binary mixtures as a function of composition at 298.15 K (reported in Table II) were fitted to the equation

$$X^E\ (X = V \text{ or } H) = x_A x_B \sum X_0^n (2x_A - 1)^n \qquad (1)$$

where X_0^n (n = 0-2) are adjustable parameters and x_A is the mole fraction of component A in the (A + B) mixtures. These parameters were evaluated by fitting $X^E/x_A x_B$ to eq 1 by the method of least squares and are recorded in Table III, together with standard deviation $\sigma(X^E)$ of X^E defined by

$$\sigma(X^E) = \left[\frac{\sum (X^E_{\text{expt}} - X^E_{\text{calcd, eq 1}})^2}{p - Q} \right]^{0.5} \qquad (2)$$

where P is the number of data points and Q is the number of adjustable parameters in eq 1.

Discussion

The present V^E data at 298.15 K for benzene (A) or *o*-xylene + *o*-chlorotoluene (B) mixtures agree within ±0.003 cm^3 mol^{-1} with the literature values (*7*). The same, however, is not true of the remaining mixtures; the literature values (*7*) are more positive than the present values, maximum deviation being 0.024 cm^3 mol^{-1} at x_A = 0.45 for *m*-xylene (A) + *o*-chlorotoluene (B) mixtures.

On the other hand while our H^E data of 298.15 K for toluene (A) + *o*-chlorotoluene (B) mixtures agree within 3.0 J mol^{-1} with the corresponding H^E data reported at 303.15 K by Otin et al. (*5*), the corresponding H^E values at 298.15 K reported (*7*) for this mixture are, however, 1/14 to 1/16 of the present as also of Otin's H^E values. Again while the reported (*7*) H^E values at 298.15 K for *m*-xylene (A) + *o*-chlorotoluene (B) agree within 4.0 J mol^{-1} with the present H^E values in the range $x_A < 0.2$, the literature values are consistently more positive than ours in the rest of the composition range, the maximum deviation being 30.0 J mol^{-1} at x_A = 0.55. The reported (*7*) H^E values for *o*-xylene or benzene (A) + *o*-chlorotoluene (B) mixtures are either more positive or more negative than the present H^E values, the maximum deviation being 30 J mol^{-1} at x_A = 0.55. This is not surprising. The small temperature coefficient of the thermistor sensor (resistance 150 Ω at 298.15 K) (*7*) enclosed in a steel capsule in an all-glass calorimeter (*17*) coupled with

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Table II. Measured V^E and H^E Data for the Various (A + B) Mixtures at 298.15 K for Various Mole Fractions, x_A, of Component A

x_A	V^E, $cm^3\ mol^{-1}$	H^E, $J\ mol^{-1}$	x_A	V^E, $cm^3\ mol^{-1}$	H^E, $J\ mol^{-1}$	x_A	V^E, $cm^3\ mol^{-1}$	H^E, $J\ mol^{-1}$	x_A	V^E, $cm^3\ mol^{-1}$	H^E, $J\ mol^{-1}$
Benzene (A) + *o*-Chlorotoluene (B)											
0.0325	0.012		0.3441		161.76	0.6750	0.162		0.8382		108.69
0.0825	0.039		0.3577	0.151		0.7210		161.94	0.8687		93.23
0.1149		63.85	0.3980	0.162		0.7280		160.00	0.8850	0.072	
0.1411	0.063		0.4006		179.16	0.7580		146.00	0.9281		53.81
0.2116	0.109		0.4749	0.177		0.7767	0.125		0.9300		51.20
0.2130		112.00	0.5635		192.90	0.7961	0.119		0.9630		27.50
0.2300	0.115		0.5930		190.10	0.8134	0.115				
0.2461		125.96	0.5955	0.183		0.8310		111.50			
Toluene (A) + *o*-Chlorotoluene (B)											
0.0312	−0.004		0.2003	−0.022		0.5123	−0.038		0.8123		−11.10
0.0516	−0.006		0.2142		−10.63	0.5188		−18.05	0.8273	−0.027	
0.0567		−3.20	0.2652	−0.030		0.6165	−0.037		0.8461		−8.82
0.1095		−5.81	0.3018	−0.030		0.6323	−0.037		0.9299	−0.013	
0.1105	−0.013		0.3047		−14.35	0.6841		−15.21	0.9568		−3.41
0.1224	−0.016		0.3583		15.73	0.7238		−14.58	0.9875	−0.002	
0.1919		−9.80	0.4291	−0.036		0.7300	−0.034				
o-Xylene (A) + *o*-Chlorotoluene (B)											
0.0502		−11.20	0.2780		−60.10	0.5177		−79.10	0.7999	−0.023	
0.0753	−0.010		0.2915		−59.71	0.5661	−0.043		0.8073	−0.021	
0.0889		−18.99	0.3250		−67.0	0.6564	−0.036		0.8125	−0.021	
0.1450	−0.020		0.3373		−66.36	0.6630		−67.00	0.8227		−39.03
0.1666		−37.31	0.3417	−0.040		0.6979		−64.03	0.9026		−21.27
0.1930		−42.50	0.3798	−0.041		0.7301	−0.031		0.9350	−0.007	
0.2002	−0.027		0.4718	−0.044		0.7920		−46.00	0.9410	−0.007	
0.2737	−0.034		0.4846		−78.83						
m-Xylene (A) + *o*-Chlorotoluene (B)											
0.1011	−0.031		0.3018	−0.080		0.6635	−0.080		0.8668	−0.038	
0.1252	−0.038		0.3258		−60.03	0.6940		−59.47	0.9057		−21.22
0.1706		−35.72	0.3858	−0.089		0.7093	−0.074		0.9154	−0.024	
0.1802	−0.056		0.4816	−0.094		0.7536	−0.062		0.9308	−0.023	
0.1909		−39.91	0.4828		−69.29	0.7900		−44.99	0.9505		−10.99
0.2511	−0.071		0.5408	−0.093		0.8270		−38.01			
0.2750		−53.48	0.6521		−62.45						
p-Xylene (A) + *o*-Chlorotoluene (B)											
0.0130	−0.003		0.1900		−43.11	0.4860		−69.90	0.7611	−0.044	
0.0385	−0.011		0.2137	−0.041		0.5122		−69.22	0.7880		−39.10
0.0492		−12.21	0.2740		−55.67	0.5300	−0.059		0.8190		−33.07
0.0801	−0.018		0.2833	−0.049		0.5841	−0.058		0.8733	−0.028	
0.0870		−20.96	0.3323		−62.18	0.6580		−56.11	0.9006		−18.60
0.0950		−23.05	0.4098	−0.058		0.6742	−0.053		0.9418	−0.014	
0.1630		−38.01	0.4780		−69.80	0.6970		−52.10	0.9958	−0.002	
0.1631	−0.035										

Table III. Values of Parameters X^n ($X = H$ or V and n = 0–2) of Eq 1 along with the Standard Deviations $\sigma(X^E)$ of X^E at 298.15 K for Various (A + B) Mixtures

system	property[a]	X_0^0	X_0^1	X_0^2	$\sigma(X^E)$
benzene (A) +	V	0.720 ± 0.006	0.189 ± 0.002	−0.1398 ± 0.002	0.001
o-chlorotoluene (B)	H	768.0 ± 4.8	119.0 ± 1.06	−97.6 ± 0.90	1.13
toluene (A) +	V	−0.150 ± 0.0038	−0.0327 ± 0.0005	−0.0223 ± 0.0003	0.001
o-chlorotoluene (B)	H	−71.2 ± 1.8	−4.763 ± 0.2	16.429 ± 0.16	0.58
o-xylene (A) +	V	−0.176 ± 0.003	0.0235 ± 0.002	0.0583 ± 0.0006	0.001
o-chlorotoluene (B)	H	−316.0 ± 3.5	−5.952 ± 0.5	114.8 ± 1.20	0.92
m-xylene (A) +	V	−0.380 ± 0.0046	0.0178 ± 0.0004	0.0684 ± 0.0013	0.001
o-chlorotoluene (B)	H	−284.0 ± 2.8	−5.9523 ± 0.41	63.69 ± 0.4801	0.65
p-xylene (A) +	V	−0.236 ± 0.004	0.00119 ± 0.0003	−0.03095 ± 0.0008	0.00
o-chlorotoluene (B)	H	−276.0 ± 3.25	41.6 ± 0.5	73.21 ± 0.82	0.84

[a] For V, X_0^0, X_0^1, X_0^2, and $\sigma(X^E)$ are in $cm^3\ mol^{-1}$. For H, X_0^0, X_0^1, X_0^2, and $\sigma(X^E)$ are in $J\ mol^{-1}$.

the fluctuations of the bath temperature would be too unreliable to properly sense the temperature changes in these mixtures for which $H^E < 80$ J mol^{-1}.

V^E and H^E values both are positive for benzene (A) + *o*-chlorotoluene (B) mixture but they become negative when benzene (A) is replaced with toluene (A) or *o*-xylene (A) or *m*-xylene (A) or *p*-xylene (A) in its binary mixtures with *o*-chlorotoluene (B). Further, for an equimolar mixture while V^E data vary in the order benzene > toluene > *o*-xylene > *p*-xylene > *m*-xylene, the H^E data vary as benzene > toluene > *m*-xylene ≈ *p*-xylene > *o*-xylene.

Registry No. Benzene, 71-43-2; toluene, 108-88-3; *o*-xylene, 95-47-6; *m*-xylene, 108-38-3; *p*-xylene, 106-42-3; *o*-chlorotoluene, 95-49-8.

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Viscosities of Pure Polyaromatic Hydrocarbons

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Experimental measurements of the viscosities of eight aromatic and polyaromatic compounds are reported for the temperature range 298–498 K. These viscosity data, with an experimental uncertainty of 0.5%, represent a substantial expansion of the data base for some materials (such as toluene) and establish a data base for such compounds as picoline and quinoline. A comparison of these data with the results of the Morris correlation and the equation of van Velzen et al. gave average errors in the 15% range.

Introduction

In the design and subsequent operation of coal conversion plants, methods for accurately predicting transport coefficients are important. For instance, it is necessary to estimate the viscosity of complex mixtures over wide ranges of concentration and temperature in order to accurately size the pumps and piping systems of these plants as well as their reaction vessels and separation units. The viscosities of polyaromatic compounds and their mixtures offer important insights into the energy relationships in organic liquid mixtures. Such information is particularly useful for compounds in the critical region, where intermolecular interactions change rapidly with temperature and pressure.

It would be logical to use generalized viscosity correlations for engineering work, when such correlations are available. However, a review of the literature reveals that predictive relationships for pure components in the temperature range well removed from the critical point are unreliable (*1*). Furthermore, the predictions generally do not apply at temperatures above the normal boiling point. This temperature range is particularly important for coal processing and near-critical extraction processes. Therefore, a program was begun to collect the data needed to develop a method for predicting viscosities for mixtures of organic pure components, particularly at temperatures above the normal boiling point. As part of this study, a laser-light-scattering technique was developed to investigate high-temperature liquid transport properties (*2*). Another facet of the program was the investigation of viscosities at temperatures below the boiling point, to provide the data required for confirmation of the laser-light-scattering method. The data base and correlations developed as a result of this work are the subjects of this report.

Solvent-based coal conversion processes produce thousands of compounds and isomers (*3*). From a list compiled by Weinstein (*4*), a series of stable representative compounds was selected for in-depth study. Only limited data have been reported for most of the pure compounds on the list, and only toluene was considered to have a satisfactory data base. Some compounds were not documented prior to this study.

Experimental Methods and Materials

The apparatus used in this study is shown schematically in Figure 1. The major component is a glass Ubbelohde viscometer manufactured by Schott Geräte (Model Series 24500). Normal viscometer operation involves drawing the sample fluid into a reservoir bulb and measuring the time required for the gravity efflux of a fixed fluid volume. This process is automated in the Schott viscometer, and fiber-optic detectors replace the visual reading. When the fluid interface passes the plane of a light beam from the transmitter to a detector unit, the voltage signal changes, starting a timer. As the interface passes a second detector, denoting the efflux of a fixed volume, the signal change stops the electronic timer. Efflux time can be determined accurately to within 0.01 s, essentially removing one of the persistent sources of experimental error in older devices. More details on the operation of capillary viscometers may be found in the literature (*5–7*).

Our experimental equipment also included a constant-temperature bath and a piping system for drawing samples into the capillary tube. Because of the temperature range involved in the experiments and the possibility of oxidation, argon (at a pressure slightly greater than ambient) was selected as a blanket gas. The temperature bath is a Haake, Model N2, recirculating unit placed in a well-insulated, cylindrical, glass container. Measurements were made at temperatures from 298 to 498 K. Over this range, it was possible to maintain a constant temperature to within 0.02 K. For convenience, water was used as the bath medium at temperatures <368 K; Dow Corning's Silicone Fluid No. 550 (phenylmethylpolysiloxane) was used at higher temperatures. A calibrated, platinum, resistance thermometer connected to a digital Fluke RTD sensor (Model 2180A) made it possible to measure temperatures accurately to within 0.1 K. The entire experimental unit (except for readout devices) was covered and heavily insulated to minimize temperature gradients. Details of equipment operation are given elsewhere (*8*).

The viscometer stand, on which the fiber-optic detectors are precisely affixed, allows the rapid interchange of viscometers. During the course of the study, several glass units were used. In all instances, the manufacturer (Schott Geräte) provided calibration constants that relate the efflux time to the kinematic viscosity.

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