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Binary Systems of Tetrachloroethylene with Benzene, Toluene, *p*-Xylene, Carbon Tetrachloride, and Cyclohexane. 2. Viscosities at 303.15 K

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Measurements of viscosities accurate to ±0.01 mP have been made for binary liquid mixtures of tetrachloroethylene (C_2Cl_4) with benzene, toluene, *p*-xylene, carbon tetrachloride, and cyclohexane at 303.15 ± 0.01 K. The values of viscosities, η, of the various mixtures have been found to fit the equation $\eta = x_1\eta_1 + x_2\eta_2 + x_1x_2[A + B(x_1 - x_2) + C(x_1 - x_2)^2]$, where η_1 and η_2 are the viscosities of the two pure liquids 1 and 2, respectively, x_1 is the mole fraction of C_2Cl_4, x_2 is the mole fraction of the aromatic hydrocarbon, CCl_4 or cyclohexane, and A, B, and C are constants characteristic of a system. The values of the quantity η^{Ex} which correspond to $\eta^{Ex} = x_1x_2[A + B(x_1 - x_2) + C(x_1 - x_2)^2]$ have been found to be negative for all the systems. For mixtures of C_2Cl_4 with aromatics at any fixed mole fraction, η^{Ex} has the following sequence: *p*-xylene > toluene > benzene.

Introduction

Recently the measurements of ultrasonic velocities and adiabatic compressibilities at 293.15 and 303.15 K, dielectric constants at 298.15 and 308.15 K, and refractive indexes at 298.15 K have been reported (*1*) for binary liquid mixtures of tetrachloroethylene (C_2Cl_4) with benzene, toluene, *p*-xylene, carbon tetrachloride, and cyclohexane. In the present program, the measurements of viscosities for these mixtures have been made at 303.15 K, and the results obtained are reported in this paper. These measurements of viscosities have been undertaken to determine whether the viscosity data throw light on the existence of specific interaction between the components of the various mixtures.

Experimental Section

Materials. The methods of purifying the various components and checking their purity have been described earlier (*1*).

Method. The viscosities of the various pure liquids and binary mixtures were measured at 303.15 ± 0.01 K, by using a kinematic viscometer described by Tuan and Fuoss (*2*) and by following the procedure described by Nath and Dubey (*3*). The measured values of the kinematic viscosities were converted to dynamic viscosities, η, by using the densities which for pure liquids were those reported earlier (*1*). The densities of mixtures were obtained from the densities of pure components and the earlier measurements on excess volumes (*4*) for their binary mixtures. The values of η thus obtained are accurate to ±0.01 mP.

Results and Discussion

The experimental values of dynamic viscosities for the various liquids and binary mixtures of C_2Cl_4 at 303.15 K are given in Table I, where x_1 refers to the mole fraction of C_2Cl_4. The values of viscosities for benzene, toluene, *p*-xylene, cyclohexane, and C_2Cl_4 at 303.15 K have been found to be 5.65, 5.22, 5.66, 8.20, and 7.98 mP, respectively, which are in good agreement with the corresponding literature (*5*) values 5.66, 5.23, 5.68, 8.20, and 7.98 mP, respectively, for the five liquids in the same order.

Table I. Experimental Values of Viscosities, η, for the Various Liquid Mixtures at 303.15 K

x_1	η, mP	x_1	η, mP
	C_2Cl_4-Benzene		
0.0000	5.65	0.5756	6.48
0.1913	5.77	0.6664	6.75
0.2749	5.84	0.7757	7.12
0.3761	6.05	0.8828	7.46
0.4668	6.24	1.0000	7.98
	C_2Cl_4-CCl_4		
0.0000	8.45	0.7629	8.00
0.3238	8.18	0.8308	7.98
0.4020	8.14	0.9128	7.97
0.5600	8.08	1.0000	7.98
0.6543	8.01		
	C_2Cl_4-Toluene		
0.0000	5.22	0.6834	6.88
0.2552	5.74	0.7448	7.06
0.3392	5.97	0.8395	7.38
0.4608	6.21	1.0000	7.98
0.5759	6.52		
	C_2Cl_4-Cyclohexane		
0.0000	8.20	0.6612	7.58
0.2317	7.77	0.7644	7.71
0.4306	7.50	0.8345	7.75
0.5117	7.51	1.0000	7.98
0.5969	7.51		
	C_2Cl_4-*p*-Xylene		
0.0000	5.66	0.6982	7.19
0.1060	5.86	0.7773	7.38
0.1121	5.88	0.8517	7.57
0.2120	6.07	1.0000	7.98
0.6339	7.04		

Table II. Values of the Least-Squares Constants A, B, and C of Eq 1 and the Standard Deviations $\sigma(\eta)$ at 303.15 K

system	A, mP	B, mP	C, mP	$\sigma(\eta)$, mP
C_2Cl_4-benzene	−2.005	0.040	−0.539	0.02
C_2Cl_4-toluene	−1.081	−0.273	0.223	0.02
C_2Cl_4-*p*-xylene	−0.374	−0.051	−0.245	0.007
C_2Cl_4-CCl_4	−0.490	0.046	−0.251	0.01
C_2Cl_4-cyclohexane	−2.346	0.206	0.938	0.03

The values of the viscosities, η, of the various mixtures of C_2Cl_4 have been found to fit the equation

$$\eta = x_1\eta_1 + x_2\eta_2 + x_1x_2[A + B(x_1 - x_2) + C(x_1 - x_2)^2] \tag{1}$$

where η_1 and η_2 are the viscosities of the two pure liquids 1 and 2, x_1 is the mole fraction of C_2Cl_4, x_2 is the mole fraction of the aromatic hydrocarbon, CCl_4 or cyclohexane, and A, B, and C are constants characteristic of a system. The values of the least-squares constants A, B, and C along with the standard deviations $\sigma(\eta)$ are given in Table II. The values of the quantity

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η^{Ex}, which refers to the deviations from a rectilinear dependence of viscosity of the mixture on mole fraction, can be discussed in the light of intermolecular interactions (*6*). The values of η^{Ex} which correspond to $\eta^{Ex} = x_1x_2[A + B(x_1 - x_2) + C(x_1 - x_2)^2]$, in the present case, have been found to be negative for all the systems (see Table II) of C_2Cl_4. For mixtures of C_2Cl_4 with aromatic hydrocarbons at any fixed mole fraction, η^{Ex} has the following sequence:

$$p\text{-xylene} > \text{toluene} > \text{benzene}$$

This béhavior of the values of η^{Ex} gives evidence of the increasing extent of interaction of C_2Cl_4 with the aromatic hydrocarbons having increasing numbers of CH_3 groups substituted in the aromatic ring. The values of η^{Ex} which have been found to be highly negative for C_2Cl_4–cyclohexane can be attributed to the fact that only the dispersion forces are present between the components of this system. The values of η^{Ex} for C_2Cl_4–CCl_4 are, however, much less negative. This, along with the trend in the values of η^{Ex} for the systems of C_2Cl_4 with benzene, toluene, and *p*-xylene, indicates the existence of specific interaction of C_2Cl_4 with CCl_4 and aromatics.

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Registry No. Tetrachloroethylene, 127-18-4; benzene, 71-43-2; toluene, 108-88-3; *p*-xylene, 106-42-3; carbon tetrachloride, 56-23-5; cyclohexane, 110-82-7.

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Substituent Effects on the Dissociation Constants and the Strength of the Hydrogen Bond in Some Azo Cresol Compounds

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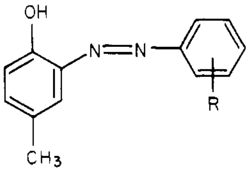
The dissociation constants of some substituted azo cresol compounds were evaluated potentiometrically and the data were explained in terms of the electronic character of the substituents. Electron-donor substituents possess higher p*K* values than the attracting groups. These values are increased by increasing the mole fraction of the dioxane solvent. The thermodynamic parameters (ΔH, ΔF, and ΔS) were evaluated and explained in terms of the strength of the intramolecular hydrogen bond. The cosolvent property was discussed and related to the molecular structure of the molecule. The phenomenon of tautomerism was visualized on the basis of infrared spectral measurements.

The azo compounds occupy an important position especially from an analytical point of view (*1–5*). In this laboratory, the structural chemistry of some azo compounds and their complexes has been determined (*6–13*). In a continuation, of these studies, we aim to focus attention on the strength of the intramolecular hydrogen bond in some substituted azo cresol compounds. The p*K*, ΔH, ΔF, and ΔS values are evaluated and the role of dioxane solvent on the behavior of these compounds is explained.

Experimental Section

The azo compounds were prepared as published elsewhere (*14*). Stock 10^{-2} M solutions of each compound were prepared by dissolving the required weight in dioxane. The exact concentration was determined potentiometrically.



R = H, *p*-NO_2, *p*-NO_2, *p*-CH_3, *p*-OCH_3,
2,4-dichloro, *o*-OCH_3

Stock 5 × 10^{-2} M KOH was prepared in different proportions of dioxane–water media. The dioxane solvent was purified as reported (*14*).

All the titration experiments were done in the following way: 50 mL of 5 × 10^{-3}–3 × 10^{-3} M of the compound containing 0.1 M KNO_3 as a supporting electrolyte thermostated in a cell at different temperatures (25–40 ± 0.5 °C) was titrated against the standard KOH solution in the presence of the desired concentration of dioxane. A stream of purified nitrogen gas was passed through the solution to eliminate CO_2 dissolved in the medium throughout the course of the titrations. A Beckman type 4500 pH meter was used for measurements and calibrated by using two buffer solutions at pH 4.01 and 9.18.

The infrared spectral measurements of a pressed KBr sample were recorded on a Unicam SP 1025.

The dissociation constant of the compound could be estimated from the titration curves where only one inflection point is apparent, indicating that only one proton is titrated. The dissociation of the ligand could be expressed as

$$HL \rightleftharpoons H^+ + L^- \qquad (1)$$

and the dissociation constant is given by the equation

$$K = [H^+][L^-]/[HL] \qquad (2)$$

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