presence of methyl substituents and molecular size.

As is evident from Tables I–IX, values of the parameter *d* are negative for all the systems except for the nitromethane–mesitylene system which has a small positive value for most of the mixtures. For all the polar solutes, *d* values increase, i.e., become less negative, as one goes from benzene to mesitylene, indicating a stronger interaction as a result of methyl subtitution in the benzene ring. This behavior is in accordance with the progressive enhancement in the polarizability of the aromatic hydrocarbons on gradual methyl substitution.

Irving has rigorously analyzed (*3*) the suitability of different equations proposed for the viscosity of liquid mixtures and found the Grunberg–Nissan equation to have the highest goodness factor for polar–nonpolar liquid mixtures. Other attempts have also been made to describe the viscosity of binary liquid mixtures in terms of those of the components and a parameter attributed to the interaction between them. Hind, McLaughlin, and Ubbelohde (*11*) suggested that

$$\eta_{12} = X_1^2\eta_1 + X_2^2\eta_2 + 2X_1X_2C \qquad (2)$$

Katti and Chaudhary (*12*), using the Eyring concept of viscosity, obtained the expression

$$\ln \eta_{12}V_{12} = X_1 \ln \eta_1V_1 + X_2 \ln \eta_2V_2 + X_1X_2/(W/RT) \quad (3)$$

where V_1 and V_2 are the molar volumes of the two components. $V_{12} = (X_1M_1 + X_2M_2)/\rho_{12}$, where ρ_{12} is the density of the mixture and M_1 and M_2 are the molecular weights of the components; *W* is the interaction energy term.

Data obtained from the present studies have been analyzed for these models and values of the parameters *C* and *W* are also given in Tables I–IX along with *d*. A perusal of the tables shows that the parameter *C* calculated by eq (2) shows the smallest variation over the whole composition range for any of the systems. Values of *C* for different aromatics for all the three polar solutes rise with the polarizability of the aromatic hydrocarbon, indicating a stronger dipole–induced-dipole interaction. Not only this, *C* values for an aromatic solvent with the different polar solutes are not that anomalous as is the case with corresponding *d* values.

W values obtained by eq 3 show almost the same, rather worse, variation over the whole composition range as *d*. Of course, *W* values for all the three polar solutes are in the order mesitylene > *p*-xylene > benzene, which is also the order of their polarizabilities. *W* values for any of the aromatic solvents with the polar solutes have again the same anomalous order as exhibited by the corresponding *d* values. In fact, one could say that the parameters *d* and *W* exhibit almost similar behavior which is not unlikely in view of logarithmic nature of both the equations. However, the Hind–McLaughlin–Ubbelohde equation seems to be the most suitable one for the viscosity data of binary mixtures of the type studied.

It may be pointed out that equations with single disposable constants, which may be regarded as interaction parameters, are simple to apply. Values of the constants may be calculated for each composition and, from the scatter of the values for the mixtures of different compositions in a series, suitability of the different equations can be compared. Inferences can be drawn regarding the extent of interaction from the values of the constant. In the case of equations containing a power series with more than one constants the viscosity data can be represented to within their scatter by taking an appropriate number of terms, which is little more than an exercise in curve fitting.

Registry No. Nitromethane, 75-52-5; nitroethane, 79-24-3; 2-nitropropane, 79-46-9; benzene, 71-43-2; *p*-xylene, 106-42-3; mesitylene, 108-67-8.

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Densities and Viscosities of Propionic Acid in Benzene, Methylbenzene, Ethylbenzene, and Propylbenzene

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The densities and the viscosities at 308.15 K were determined for the systems propionic acid (PA) + benzene (B), + methylbenzene (MB), + ethylbenzene (EB), and + propylbenzene (PB). The excess viscosities and excess molar volumes were calculated from the experimental results. The excess molar volumes show a slight consistent trend toward more positive values as the length of the hydrocarbon side chain of the benzene ring increases. The results suggest the presence of specific interactions.

As part of our studies on physicochemical properties of binary liquid mixtures with carboxylic acids (*1–3*) (carboxylic acid as the main component), we have obtained the excess molar volumes and excess viscosities from the measured densities and the viscosities of the following binary liquid mixtures: propionic acid (PA) + benzene (B), + methylbenzene (MB), + ethylbenzene (EB), and + propylbenzene (PB) at 308.15 K and under atmospheric pressure. The results are communicated here.

Experimental Section

Densities were measured with a 18-mL bicapillary pycnometer having a capillary diameter of 0.85 mm. The pycnometer was calibrated by using double distilled water (density 994.06 kg m^{-3} at 308.15 K). All weighings were done on a Mettler

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Table I. Densities of Pure Liquids at 308.15 K

component	ρ, kg m^{-3} present study	ρ, kg m^{-3} lit.	ref
propionic acid	978.2	978.0	*6*
benzene	863.0	862.9	*5*
methylbenzene	853.1	852.9	*5*
ethylbenzene	853.8	853.2	*5*
propylbenzene	849.4	848.1	*5*

balance (±0.05 mg). The necessary buoyancy correction was applied. The density values were reproducible within ±0.2 kg m^{-3}. A thermostatically controlled water bath capable of maintaining the temperature constant to ±0.02 K was used in the studies.

Viscosities of the pure liquids and the liquid mixtures were determined with a modified Ostwald viscometer. The time of efflux was measured with a precalibrated Rocar stop watch capable of recording ±0.1 s. The viscometer was always kept in a vertical position in a water thermostat at 308.15 ± 0.02 K. The efflux time for water at 308.15 K was about 302 s. The efflux time was kept relatively long to minimize the kinetic energy corrections. A series of efflux times were recorded for each mixture and the viscosity was calculated from the average efflux time t and density ρ by using the equation

$$\eta/\rho = at - b/t \qquad (1)$$

where a and b are the characteristic constants of the viscometer. The experiments were repeated till at least three successive viscosity measurements agreed to $\pm 0.05 \times 10^{-4}$ kg m^{-1} s^{-1}. The constants a and b were determined by using water and benzene as the calibrating liquids, and the kinetic energy corrections were calculated. The corrections are found negligible. The viscosity values of water and benzene used in our calibration were taken from the literature (*4*).

Propionic acid, Fluka (99%), was dried over anhydrous sodium sulfate and fractionally distilled. The fraction distilling at 412.15–414.15 K was collected and refractioned over potassium permanganate. The middle fraction distilling at 413.85 K at 760 mm was collected and used in these experiments.

Benzene, methylbenzene, ethylbenzene, and propylbenzene supplied by BDH (AnalaR reagent grade) were purified according to standard procedure (*5*). The purity of each solvent was ascertained by the constancy of the boiling temperature during final distillation and by comparing the density with the literature value (*5*, *6*) (Table I).

Mixtures were prepared by mixing weighed amounts of the pure liquids. The mixing bottle (*7*) was used to minimize evaporation loses.

Results

The excess functions were calculated by using the following equations

$$\Delta\eta = \eta - (x_1\eta_1 + x_2\eta_2) \qquad (2)$$

$$V^E = V - (x_1V_1 + x_2V_2) \qquad (3)$$

where η, η_1, and η_2 are the viscosities of the mixture and of the pure components. V, V_1, and V_2 are molar volumes of the mixture and of the pure components. x_1 is the mole fraction of the propionic acid.

The molar volume V of the mixture is defined by

$$V = \frac{x_1M_1 + x_2M_2}{\rho} \qquad (4)$$

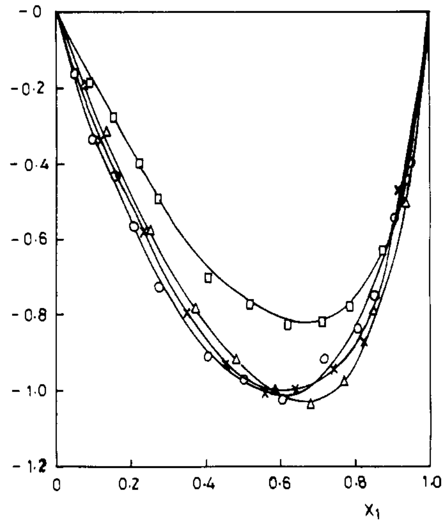

Figure 1. Excess viscosities of mixing at 308.15 K for the mixtures of propionic acid (PA) + benzene (○); + methylbenzene (×); + ethylbenzene (△); + propylbenzene (□).

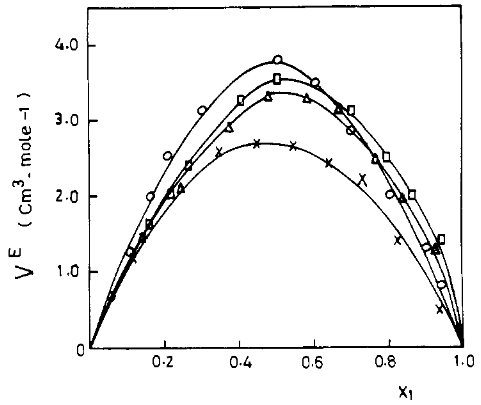

Figure 2. Excess volume of mixing at 308.15 for the mixtures of propionic acid (PA), + benzene (○), + methylbenzene (×); + ethylbenzene (△); + propylbenzene (□).

where M_1 and M_2 are the molecular weights of the components and ρ is the density of the solution.

The experimental mole fractions, densities, viscosities, and the calculated excess viscosities and excess molar volumes are listed in Table II.

Each set of results is fitted to the following empirical equation

$$X^E = x_1x_2[A_0 + A_1(x_1 - x_2) + A_2(x_1 - x_2)^2] \qquad (5)$$

where X^E represents property under consideration. 1 and 2 represent the pure components, and A_0, A_1, and A_2 are constants. The method of least squares was used to determine values of the constants for each mixture. The values of these constants along with the standard deviation (σ) defined by

$$\sigma = [\sum(X^E_{\text{obsd}} - X^E_{\text{calcd}})^2/n - 3]^{1/2} \qquad (6)$$

are given in Table III. Equation 5 fits the data within the allowed uncertainties. The few minor deviations seem random rather than systematic. Figures 1 and 2 show respectively the plots of η^E and V^E versus mole fraction of propionic acid.

Discussion

Viscosity decreases to a greater extent on the initial addition of hydrocarbon to propionic acid. This behavior is characteristic of systems in which at least one of the components exhibits intramolecular hydrogen bonding (*8*). It is known that intermolecular hydrogen bonding exists in propionic acid (*9*). The

Table II. Experimental Values of Density (ρ), Viscosity (η), and the Calculated Values of Excess Viscosities and Excess Molar Volume (V^E) for the Systems at 308.15 K

x_1[a]	ρ, kg m^{-3}	$10^4\eta$, kg m^{-1} s^{-1}	$10^4\Delta\eta$, kg m^{-1} s^{-1}	V^E, cm^3 mol^{-1}
Propionic Acid + Benzene				
0.0000	863.0	5.518	0.000	0.0000
0.0534	867.5	5.535	−0.163	0.0671
0.1063	872.1	5.551	−0.326	0.1258
0.1575	876.5	5.517	−0.435	0.1978
0.2079	881.0	5.677	−0.559	0.2566
0.3318	891.2	5.849	−0.722	0.3122
0.4118	901.8	5.998	−0.910	0.3229
0.5132	912.5	6.282	−0.965	0.3809
0.6132	924.3	6.564	−1.025	0.3503
0.7107	936.7	7.012	−0.905	0.2860
0.8085	949.8	7.408	−0.839	0.2009
0.8566	955.9	7.662	−0.748	0.2041
0.9045	963.0	8.033	−0.539	0.1313
0.9524	969.2	8.347	−0.387	0.1454
1.0000	978.2	8.894	0.000	0.0000
Propionic Acid + Methylbenzene				
0.0000	853.1	5.248	0.000	0.0000
0.1231	863.2	5.358	−0.340	0.1202
0.2366	873.9	5.532	−0.579	0.1650
0.3487	885.1	5.721	−0.798	0.2663
0.4523	896.2	5.970	−0.928	0.2633
0.5546	909.0	6.271	−1.000	0.2045
0.6523	921.2	6.628	−0.998	0.2403
0.7435	934.0	7.020	−0.939	0.2269
0.8320	948.0	7.411	−0.870	0.1422
0.9187	963.0	8.128	−0.470	0.0458
1.0000	978.2	8.894	0.000	0.0000
Propionic Acid + Ethylbenzene				
0.0000	853.8	5.797	0.000	0.0000
0.1393	863.9	5.916	−0.312	0.1431
0.2634	874.3	6.031	−0.582	0.2088
0.3813	885.1	6.196	−0.782	0.2897
0.4881	896.3	6.386	−0.922	0.3373
0.5891	908.3	6.621	−1.001	0.3313
0.6835	920.9	6.881	−1.033	0.3133
0.7694	934.0	7.210	−0.970	0.2493
0.8518	947.7	7.666	−0.769	0.1990
0.9275	961.8	8.175	−0.495	0.1320
1.0000	978.2	8.894	0.000	0.0000
Propionic Acid + Propylbenzene				
0.0000	849.4	7.001	0.000	0.0000
0.0799	854.8	6.969	−0.193	0.0464
0.1548	860.0	7.021	−0.273	0.1377
0.2233	865.1	7.031	−0.393	0.1993
0.2750	869.4	7.037	−0.485	0.2365
0.4110	882.0	7.084	−0.695	0.2896
0.5190	983.4	7.218	−0.766	0.3561
0.6192	906.0	7.357	−0.817	0.3358
0.7099	919.1	7.530	−0.815	0.3042
0.7906	932.6	7.717	−0.781	0.2451
0.8664	946.6	8.012	−0.629	0.2055
0.9357	961.5	8.334	−0.438	0.1151
1.0000	978.2	8.894	0.000	0.0000

[a] Mole fraction of propionic acid.

Table III. Parameters of Eq 5 and Standard Deviation (σ) of Experimental Values at 308.15 K[a]

system	function	A_0	A_1	A_2	σ
PA + B	$\Delta\eta$	−0.370	−0.217	−0.229	0.007
	V^E	1.292	0.356	0.736	0.044
PA + MB	$\Delta\eta$	−0.392	−0.202	−0.132	0.004
	V^E	1.072	−0.106	−0.253	0.034
PB + EB	$\Delta\eta$	−0.372	−0.258	−0.173	0.003
	V^E	1.250	0.364	0.346	0.019
PA + PB	$\Delta\eta$	−0.286	−0.238	−0.249	0.006
	V^E	1.340	0.562	−0.026	0.019

[a] Units: $\Delta\eta$, kg m^{-1} s^{-1}; V^E, cm^3 mol^{-1}.

minimum observed in η^E (cf. Figure 1) at approximately x_1 = 0.60 suggests that addition of benzene results in the breakdown of the intramolecular hydrogen bonding in propionic acid.

The differences in molecular size and interference with the dipole–dipole interactions (hydrogen-bond breaking) lead to excess volumes. Similar reports were made by Prigogine (*10*). The observed values of V^E are in the sequence PA + benzene > PA + propylbenzene > PA + ethylbenene > PA + methylbenzene.

The observed trends in the properties measured were therefore ascribed to the breakdown of the intramolecular hydrogen bonding in priopionic acid and the n–π interaction between propionic acid and hydrocarbon.

Glossary

V^E	excess volume
$\Delta\eta$	excess viscosity
ρ	density
η	viscosity
V	molar volume of solution
M	molecular mass
x	mole fraction
R	gas constant

Superscript

E	excess

Subscript

1,2	component number in mixtures

Registry No. PA, 79-09-4; B, 71-43-2; MB, 108-88-3; EB, 100-41-4; PB, 103-65-1.

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