tylamine at the three temperatures measured in this work. Figure 2 depicts a similar representation for the system *n*-amylamine + methylcyclohexane.

As can be seen from Figure 2, for the system *n*-butylamine + methylcyclohexane the curves of the heats of mixing for the three temperatures virtually coincide at the *n*-butylamine-rich extreme of the composition range. A study of the more sensitive representation of $\Delta H/x_1x_2$ versus x_2 showed that the last three points of the *n*-butylamine-rich extreme of the composition range at 298.15 K crossed the curve corresponding to 308.15 K. Calculations showed that an error in the mole fraction of 0.0004 was enough to produce this effect. Since this magnitude of error in the mole fraction is well within the experimental error of our measurements, the last two points of the *n*-butylamine-rich extreme of the composition range were eliminated from the smoothing of the data at this temperature.

For the system *n*-butylamine + toluene, Figure 1 shows a larger separation of the curves at the three temperatures and the above problem was not encountered. Figure 3 presents the curves of $\Delta H/x_1x_2$ versus x_2 for this system.

Glossary

A, B, C	coefficients of the Redlich–Kister polynomial, J/mol
T	temperature, K
x	mole fraction
ΔH	heat of mixing per mole of mixture, J/mol

Subscripts

1	*n*-butylamine
2	toluene or methylcyclohexane

Registry No. *n*-Butylamine, 109-73-9; toluene, 108-88-3; methylcyclohexane, 108-87-2.

Literature Cited

(1) Abusleme, J. A.; Vera, J. H. *Fluid Phase Equilib.* **1985**, *22*, 123–138.
(2) Abusleme, J. A.; Vera, J. H. *Can. J. Chem. Eng.* **1985**, *63*, 845–849.
(3) Siman, J. E.; Vera, J. H. *Can. J. Chem. Eng.* **1979**, *57*, 355–362.
(4) Chamblain, J.-F.; M. Eng. Thesis, McGill University, 1985.
(5) Christensen, J. J.; Hanks, R. w.; Izatt, R. M. *Handbook of Heats of Mixing*; Wiley Interscience: New York, 1982; p 1124.
(6) Hammond, L. W.; Howard, K. S.; McAllister, R. A. *J. Phys. Chem.* **1958**, *62*, 637–639.
(7) Kyle, B. G.; Reed, T. M. *J. Am. Chem. Soc.* **1958**, *80*, 6170–6177.
(8) Letcher, T. M.; Bayles, J. W. *J. Chem. Eng. Data* **1971**, *16*, 266–271.

Received for review May 12, 1986. Accepted July 13, 1987. We are grateful to NSERC, Canada, for financial support of this study and to Tsinghua University and the Government of P.R. China for financial support to Y.Z.

Viscosities of Some Binary Ethyl Acetate Mixtures at 313.15 K

M. V. Rathnam

Bandodkar College of Science, Thane 400 601, Bombay, India

Viscosity coefficient measurements at saturation pressure are reported for ethyl acetate + *o*-xylene, ethyl acetate + *p*-xylene, ethyl acetate + *p*-dioxane, and ethyl acetate + tetrahydrofuran over the entire range of composition at 313.15 K. The values of mixture viscosity have been calculated for different compositions by the application of the Katti and Chaudhri equation. It was found that the experimental viscosities are in reasonable agreement with the calculated viscosities and within the uncertainty limits of ±0.003 cP. The absolute magnitude of the probable error does not change much from system to system.

Introduction

In recent years there has been considerable advancement in the experimental investigation of the excess thermodynamic properties of liquid mixtures. A survey of the literature shows that very few attempts (*1*, *2*) have been made to study viscosities of binary liquid mixtures containing esters. Therefore it was thought worthwhile to study viscosities of binary solutions of esters in polar and nonpolar solvents. Hence in the present program the measurements of viscosities for binary liquid mixtures of ethyl acetate with *o*-xylene, *p*-xylene, *p*-dioxane, and tetrahydrofuran have been made at 313.15 K.

Experimental Section

Ethyl acetate (BHD, AnalaR), *o*-xylene, *p*-xylene, *p*-dioxane, and tetrahydrofuran all (BDH, AnalaR) were purified as per procedure given by Riddick and Bunger (*3*). Xylenes were freed from thiophene by shaking with sulfuric acid; the samples so obtained were washed with water followed by subsequent washing with sodium hydroxide and distilled water, dried thoroughly over anhydrous calcium chloride, and fractionally distilled twice. *p*-Dioxane was first refluxed with sodium hydroxide and then with sodium till free from peroxide and finally fractionally distilled over sodium. Tetrahydrofuran was treated with anhydrous ferrous sulfate, refluxed with potassium hydroxide for several hours and finally distilled over sodium. All the chemicals were distilled before use. Further, the purity of these samples was tested by measuring their densities, viscosities, and refractive indices at 303.15 K, which compared well with the literature values (*3*, *4*, *7*), Table I.

Table I. Physical Properties of Pure Components in the Present Work and in the Literature at 303.15 K

	density (d), g cm^{-3}		viscosity (η), cP		refractive index (n_D)	
component	exptl	lit.[a]	exptl	lit.[a]	exptl	lit.[a]
ethyl acetate	0.8885	0.8885	0.403	0.400	1.3680	1.3673
o-xylene	0.8717	0.8716 0.8717[b]	0.693	0.693	1.5004	1.5003
p-xylene	0.8527	0.8523	0.564	0.568 0.566[b]	1.4908	1.4907
p-dioxane	1.0227	1.0223	1.086	1.087	1.4180	1.4180
tetrahydrofuran	0.8788	0.8790[c]	0.438	0.438[b]	1.4028	1.4028[b]

[a] Reference *4*. [b] Reference *3*. [c] Reference *7*.

Kinematic viscosities of the pure liquids and mixtures at different concentrations were determined at 313.15 K by using an Ubbelohde viscometer (*5*). The viscometer was calibrated against water and benzene. The time of efflux of a constant volume of liquid through the capillary was measured with the help of a precalibrated RACER stop watch accurate to ±0.1 s. The viscometer was always kept in a vertical position in a water thermostat. The thermostat bath was controlled to within ±0.01 °C. Once the temperature was stabilized the flow times for mixtures at different concentrations were measured. Stabilization was considered to be achieved when at least 4–5

0021-9568/88/1733-0014$01.50/0 © 1988 American Chemical Society

Table II. Molar Volume (V), Kinematic Viscosity (v), Absolute Viscosity (η), Excess Viscosity (η^E), and Interaction Energy (W_{visc}) for Binary Mixtures of Ethyl Acetate (Component 1) at 313.15 K

X_1	V, cm^3 mol^{-1}	v, St	η, cP	η (eq 3), cP	η^E	W_{visc}, J mol^{-1}
		Ethyl Acetate + *o*-Xylene				
0.0000	123.0	0.726	0.627			
0.1789	118.9	0.662	0.573	0.573	−0.008	
0.2056	118.4	0.653	0.565	0.564	−0.009	
0.4079	113.9	0.585	0.508	0.508	−0.014	
0.5023	111.8	0.556	0.483	0.483	−0.014	114.0
0.5988	109.6	0.528	0.459	0.459	−0.014	
0.8618	105.0	0.471	0.411	0.411	−0.009	
0.9583	101.3	0.431	0.378	0.378	−0.002	
1.0000	100.5	0.421	0.369			
		Ethyl Acetate + *p*-Xylene				
0.0000	125.9	0.608	0.513			
0.1645	121.7	0.574	0.487	0.490	−0.002	
0.2063	120.6	0.566	0.481	0.481	−0.002	
0.4077	115.6	0.526	0.450	0.450	−0.004	
0.5061	113.1	0.507	0.436	0.436	−0.005	110.8
0.5991	110.8	0.491	0.422	0.422	−0.004	
0.8016	105.5	0.455	0.395	0.395	−0.003	
0.9585	101.7	0.428	0.374	0.374	−0.001	
1.0000	100.5	0.421	0.369			
		Ethyl Acetate + *p*-Dioxane				
0.0000	87.1	0.929	0.939			
0.1779	86.4	0.753	0.768	0.771	−0.070	
0.2090	89.9	0.732	0.717	0.721	−0.103	
0.4050	92.5	0.612	0.584	0.586	−0.124	
0.5144	93.9	0.563	0.527	0.527	−0.119	−995.2
0.6020	95.1	0.529	0.490	0.488	−0.106	
0.7994	97.8	0.469	0.423	0.418	−0.060	
0.9411	102.0	0.435	0.376	0.373	−0.027	
1.0000	100.5	0.421	0.369			
		Ethyl Acetate + Tetrahydrofuran				
0.0000	83.2	0.460	0.399			
0.1718	86.2	0.447	0.387	0.387	−0.006	
0.2044	86.7	0.442	0.386	0.385	−0.009	
0.4059	90.3	0.431	0.376	0.375	−0.011	
0.5072	92.1	0.428	0.372	0.372	−0.012	−258.5
0.6002	93.7	0.424	0.370	0.370	−0.011	
0.7996	97.1	0.422	0.369	0.368	−0.006	
0.9583	100.1	0.421	0.368	0.367	−0.002	
1.0000	100.5	0.421	0.369			

consecutive readings gave the same flow time. The sample was then removed, the viscometer was dried, and another sample was introduced. This procedure was repeated for all mixtures. Flow times for water as well as for pure solvents and their mixtures were quite consistent during the entire period of measurement. The flow time for water at 313.15 K was about 178 s. The viscosities thus estimated here are accurate to within ±0.2%. The densities (*6*) were measured at 313.15 K in a previously calibrated pycnometer. The pycnometer was maintained at 313.15 ± 0.01 K in a water thermostat controlled to within ±0.01 °C. The values of densities thus estimated are reproducible to ±0.0002 units.

Results and Discussion

Table III. Values of Parameters for Eq 2 and the Standard Deviation σ at 313.15 K

system	a_0	a_1	a_2	$\sigma(\eta^E)$
ethyl acetate + *o*-xylene	−0.0575	−0.0013	0.0043	0.000
ethyl acetate + *p*-xylene	−0.0181	0.0122	0.0073	0.002
ethyl acetate + *p*-dioxane	−0.4792	0.2101	−0.0608	0.001
ethyl acetate + tetrahydrofuran	−0.0466	0.0146	−0.0001	0.001

The experimental values of kinematic viscosities (v) of ethyl acetate + *o*-xylene, + *p*-xylene, + *p*-dioxane, and + tetrahydrofuran at 313.15 K are reported in Table II. The kinematic viscosities (v) were converted into absolute viscosities (η) by multiplying the former with density. The excess viscosities η^E calculated by using the relation

$$\eta^E = \eta_{12} - (x_1\eta_1 + x_2\eta_2) \tag{1}$$

were fitted to the empirical relation

$$\eta^E = x(1 - x)[a_0 + a_1(2x - 1) + a_2(2x - 1)^2] \tag{2}$$

where x denotes the mole fraction of ethyl acetate and a_0, a_1, and a_2 are constants. The values of these constants along with their standard deviation are given in Table III.

The mixture viscosities have also been calculated by using the Katti and Chaudhri equation.

$$\ln \eta_{12}v_{12} = x_1 \ln \eta_1 v_1 + x_2 \ln \eta_2 v_2 + x_1 x_2 \frac{W_{visc}}{RT} \tag{3}$$

The calculated values of the mixture viscosities and molar volumes from the density data (*6*) calculated by using the relation

$$V = (M_1x_1 + M_2x_2)/d_{12} \tag{4}$$

at different concentrations for each mixture are shown in Table II. W_{visc} calculated at equimolar concentration for each system is presented in the last column of Table II. The agreement between the observed and calculated viscosities for all the mixtures over the whole range of concentrations is close and within the experimental error.

Acknowledgment

The author thanks Dr. T. S. Rao, University of Poona, for his suggestions and discussion and appreciates the referees also for their valuable constructive comments.

Registry No. Ethyl acetate, 141-78-6; *o*-xylene, 95-47-6; *p*-xylene, 106-42-3; *p*-dioxane, 123-91-1; tetrahydrofuran, 109-99-9.

Literature Cited

(1) Katti, P. K.; Chaudhri, M. M. *J. Chem. Eng. Data* **1964**, *9*, 422.
(2) Aminabhavi, T. M.; Patel, R. C.; Bridger, K. *J. Chem. Eng. Data* **1982**, *27*, 125.
(3) Riddick, J. R.; Bunger, W. B. *Organic Solvents: Physical Properties and Methods of Purification*, 3rd ed.; Wiley Interscience: New York, 1970; Vol. 2.
(4) Timmermans, J. *Physico-Chemical Constants of Pure Organic Compounds*; Elsevier: Amsterdam, 1950.
(5) Ubbelohde, L. *Ind. Eng. Chem. Anal. Ed.* **1937**, *9*, 85.
(6) Rathnam, M. V. *Indian J. Chem.* **1986**, *25A*, 1145–1146.
(7) Jain, D. V. S.; Sidhu, R. S. *J. Chem. Thermodyn.* **1984**, *16*, 111.

Received for review May 19, 1986. Revised October 20, 1986. Accepted July 7, 1987.