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Volume of Mixing, Speed of Sound, and Viscosity of Butyl Acetate with Xylenes at 303.15 K

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The volume of mixing, speed of sound, and viscosity of binary liquid mixtures composed of butyl acetate + *o*-xylene, + *m*-xylene, and + *p*-xylene have been measured at 303.15 K. The excess volumes and deviations in isentropic compressibility and viscosity are discussed in terms of molecular interaction between like and unlike components.

Introduction

Mixtures of organic liquids often show strong deviations from ideality as regards density and viscosity. Predicting deviations is important in industrial fields, where solvent mixtures are used.

A survey of the literature showed that excess volumes of binary mixtures of butyl acetate with aromatic hydrocarbons (*1*), alkanes (*2*), alcohols (*3*), 2−hexanone (*4*), and chloroethanes and -ethenes (*5*). The speed of sound of binary mixtures of butyl acetate with aromatic hydrocarbons (*6*) and viscosities of binary mixtures of butyl acetate with alkanes (*2*), 2-hexanone (*4*), and carbon tetrachloride (*7*) have been measured. However, no systematic effort has been made to study the interaction between butyl acetate with xylenes at 303.15 K. We report the experimental volume of mixing, speed of sound, and viscosities of three binary liquid mixtures. The mixtures are butyl acetate + *o*-xylene, + *m*-xylene, and + *p*-xylene at 303.15 K. The study was undertaken to examine the effect of V^E_m of the substituents at the ortho, meta, and para positions of the benzene ring with mixtures with acetates.

Experimental Section

Materials. Butyl acetate (AR) was purified by the standard method described by Vogel (*8*). Butyl acetate was dried with anhydrous magnesium sulfate and fractionally distilled. AR grade samples of *o*-xylene, *m*-xylene, and *p*-xylene were purified by the method described by Rambabu et al. (*9*). The purities of all substances were better than 99.95 mass %, found by GLC analysis. The purities of the samples were confirmed by comparing the densities and boiling points with those reported in the literature (*10*). The densities were measured using a bicapillary pycnometer which gave an accuracy of 5 parts in 10^5. The boiling points were measured using a Swiestoslawski type ebulliometer (*11*), which gave an accuracy of ±0.2 K. The measured values are included in Table 1 along with the literature values.

Procedure. Excess volumes were measured directly using the batch dilatometer technique described earlier (*12*). Three additional dilatometers having a large difference in the size of the limbs were used for measurements at the ends of the mole fraction range. The V^E values are reproducible to ±0.003 $cm^3 \cdot mol^{-1}$. A thermostatically controlled well-stirred water bath with temperature controlled to ±0.01 K was used for all the measurements. The composition of the mixture was calculated from the mass of the components, and the uncertainty in the mole fraction was estimated to be less than $\pm 5 \times 10^{-4}$.

Table 1. Boiling Points T_b, Densities ϱ, and Viscosities η of Pure Components at 303.15 K

	T_b/K		$\varrho/(g \cdot cm^{-3})$		$\eta/(mPa \cdot s)$	
component	exptl	lit. (*10, 11*)	exptl	lit. (*10, 11*)	exptl	lit. (*10, 11*)
butyl acetate	399.1	399.3	0.871 27	0.871 29	1.384	1.383
o-xylene	417.7	417.6	0.871 75	0.871 74	0.693	0.693
m-xylene	412.2	412.3	0.855 80	0.855 81	0.547	0.547
p-xylene	411.6	411.3	0.852 27	0.852 25	0.567	0.567

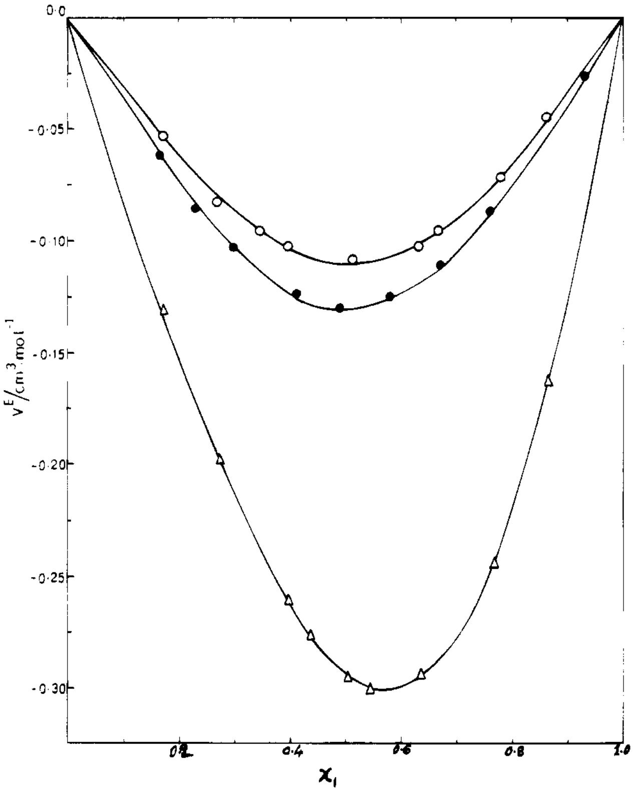

Figure 1. Excess volumes of butyl acetate (1) + *o*-xylene (2) (○), + *m*-xylene (2) (●), and + *p*-xylene (2) (△) at 303.15 K versus the mole fraction of butyl acetate.

The liquid mixtures were recovered from the dilatometers using a hypodermic syringe, and used to measure the speed of sound and viscosity. Speeds of sound were measured with a single-crystal ultrasonic interferometer

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Table 2. Density, ϱ, Volume of Mixing, V^E, Speed of Sound, U, Isentropic Compressibility, K_s, and Viscosity, η, at 303.15 K

x_1	ϕ_1	ϱ/(g·cm^3)	V^E/(cm^3·mol^{-1})	u/ms^{-1}	K_s/TPa^{-1}	η/(mPa·s)
		Butyl Acetate (1) + o-Xylene (2)				
0.0000	0.0000	0.871 75		1329	651	0.693
0.1704	0.1875	0.872 03	−0.053	1301	678	0.803
0.2732	0.2915	0.872 18	−0.082	1284	696	0.871
0.3489	0.3697	0.872 23	−0.095	1276	704	0.920
0.4037	0.4256	0.872 25	−0.103	1267	714	0.958
0.5168	0.5393	0.872 24	−0.109	1250	734	1.038
0.6323	0.6530	0.872 14	−0.103	1232	755	1.119
0.6625	0.6824	0.872 09	−0.096	1226	763	1.142
0.7804	0.7955	0.872 85	−0.072	1206	787	1.226
0.8672	0.8773	0.871 63	−0.045	1197	804	1.288
1.0000	1.0000	0.872 27		1175	831	1.384
		Butyl Acetate (1) + m-Xylene (2)				
0.0000	0.0000	0.855 80		1303	690	0.547
0.1666	0.1768	0.858 98	−0.063	1288	702	0.661
0.2307	0.2437	0.860 16	−0.085	1281	709	0.704
0.3015	0.3168	0.861 41	−0.104	1273	717	0.758
0.4094	0.4268	0.863 25	−0.123	1258	732	0.846
0.4958	0.5137	0.864 64	−0.130	1246	745	0.922
0.5808	0.5981	0.865 90	−0.125	1234	759	0.998
0.6704	0.6860	0.867 16	−0.111	1221	774	1.078
0.7604	0.7732	0.868 34	−0.086	1206	792	1.162
0.9306	0.9351	0.870 45	−0.026	1184	819	1.318
1.0000	1.0000	0.872 27		1175	831	1.384
		Butyl Acetate (1) + p-Xylene (2)				
0.0000	0.0000	0.852 27		1292	704	0.567
0.1785	0.1887	0.856 74	−0.131	1277	717	0.567
0.2766	0.2904	0.859 12	−0.198	1264	729	0.604
0.3998	0.4161	0.861 92	−0.260	1250	742	0.688
0.4422	0.4590	0.862 84	−0.276	1246	746	0.724
0.5026	0.5196	0.864 11	−0.294	1239	754	0.781
0.5559	0.5726	0.865 17	−0.302	1232	762	0.834
0.6345	0.6501	0.866 58	−0.294	1220	775	0.920
0.7637	0.7757	0.868 62	−0.242	1203	795	1.075
0.8673	0.8749	0.869 96	−0.161	1189	813	1.209
1.0000	1.0000	0.871 27		1175	831	1.384

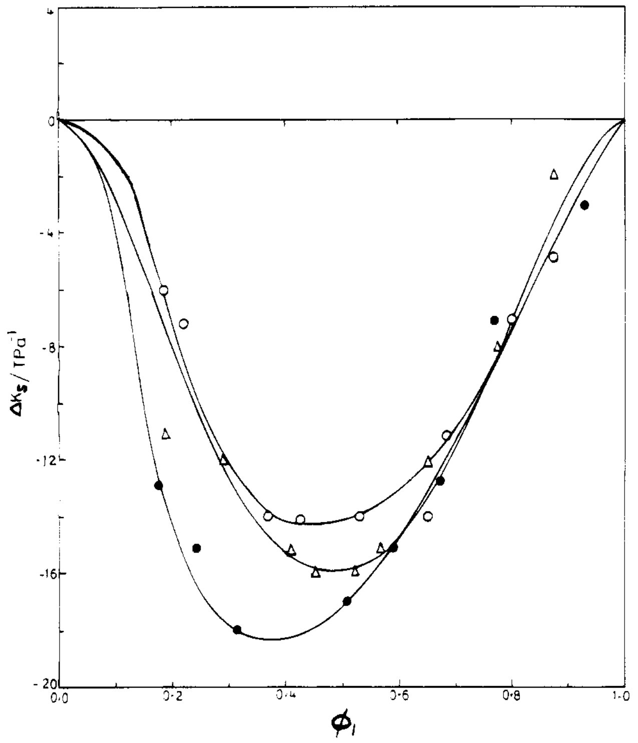

Figure 2. Deviation in the isentropic compressibility of butyl acetate + o-xylene (2) (○), + m-xylene (2) (●), and + p-xylene (2) (△) at 303.15 K versus the volume fraction of butyl acetate.

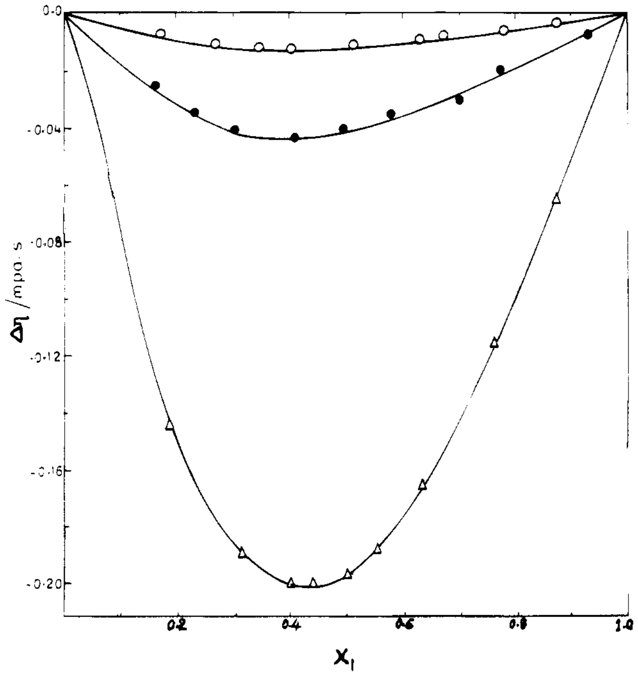

Figure 3. Deviation in viscosity for butyl acetate + o-xylene (2) (○), + m-xylene (2) (●), and + p-xylene (2) (△) at 303.15 K versus the mole fraction of butyl acetate.

(Mittal Enterprises, New Delhi) at a fixed frequency of 3 MHz. The values are reproducible to ±0.1%.

Viscosities were measured using a suspended level Ubbelohde viscometer. The viscometer was calibrated at 303.15 K using distilled water. The viscometer constant K was calculated from the viscosity η_w, density ϱ_w, and flow time, t_w, of water using the relation $K = \eta_w/(t_w\varrho_w)$. An average of 10 measurements which did not differ by more than 0.005 cm^2·s^{-2} was taken as the K value. An electronic stopwatch capable of measuring time to ±0.015 s was used for time measurements. Kinetic energy corrections were negligible. The estimated error in viscosity is $\pm 5 \times 10^{-4}$ mPa·s. The performance of the viscometer was assessed by measuring and comparing the viscosities of the pure components with the values reported in the literature (*10, 11*).

Results

Experimental volume of mixing (V^E) data, the speed of sound (u), and viscosity (η) are given in Table 2 and in Figures 1–3, respectively. The V^E values are used to compare the density (ϱ) of mixtures from the equation

$$\varrho = \frac{x_1M_1 + x_2M_2}{x_1V_1 + x_2V_2 + V^E_m} \tag{1}$$

where x_1 and x_2 are the mole fractions, M_1 and M_2 are molar masses, and V_1 and V_2 are molar volumes of butyl acetate (1) and xylenes (2), respectively. Speeds of sound (u) along with the density data are used to calculate the isentropic compressibility (K_s) and the deviation in isentropic compressibility (ΔK_s):

$$K_s = 1/u^2\varrho \tag{2}$$

$$\Delta K_s = K_s - \phi_1K_{s1} - \phi_2K_{s2} \tag{3}$$

where ϕ_1 and ϕ_2 are the ideal volume fractions of components 1 and 2, respectively, and K_s, K_{s1}, and K_{s2} are the isentropic compressibilities of the mixture and components 1 and 2, respectively. The deviation in the viscosity from

Table 3. Values of the Parameters of Eq 7 and Standard Deviations at 303.15 K

Y	a_0	a_1	a_2	$\sigma(Y)$
Butyl Acetate (1) + *o*-Xylene (2)				
$V^E/(\mathrm{cm^3 \cdot mol^{-1}})$	−0.441	−0.028	0.124	0.001
$\Delta K_s/(\mathrm{TPa^{-1}})$	−58.804	−9.034	37.098	2
$\Delta\eta/(\mathrm{mPa \cdot s})$	−0.052	0.016	0.012	0.001
Butyl Acetate (1) + *m*-Xylene (2)				
$V^E/(\mathrm{cm^3 \cdot mol^{-1}})$	−0.517	−0.010	0.150	0.001
$\Delta K_s/(\mathrm{TPa^{-1}})$	−67.189	26.335	−5.705	1
$\Delta\eta/(\mathrm{mPa \cdot s})$	−0.160	0.049	−0.004	0.003
Butyl Acetate (1) + *p*-Xylene (2)				
$V^E/(\mathrm{cm^3 \cdot mol^{-1}})$	−1.171	−0.356	0.062	0.004
$\Delta K_s/(\mathrm{TPa^{-1}})$	−62.668	18.769	35.587	1
$\Delta\eta/(\mathrm{mPa \cdot s})$	−0.793	0.281	−0.017	0.003

a mole fraction average is given by

$$\Delta\eta = \eta_m - (x_1\eta_1 + x_2\eta_2) \tag{4}$$

where η_m is the viscosity of the mixture and η_1 and η_2 are the viscosities of butyl aetate and xylenes, respectively. V^E as a function of mole fraction is shown in Figure 1. The variation of ΔK_s with volume fraction and of $\Delta\eta$ with mole fraction is given in Figures 2 and 3, respectively.

Discussion

The composition dependence of the volume of mixing, deviation in isentropic compressibility, and viscosity deviation are correlated by the Redlich–Kister polynomial (*13*)

$$Y = x_1x_2\sum_{i=0}^{2} a_i(x_1 - x_2)^i \tag{5}$$

where if Y is the volume of mixing or viscosity deviation, the composition is in mole fraction, and if y is the deviation in compressibility, the composition is in volume fraction, and a_i are the adjustable parameters and are evaluated from the least-squares method. The values of the parameters along with the standard deviation are given in Table 3. Values of σ were obtained from the equation

$$\sigma = \left[\frac{\sum(Y_{\mathrm{exptl}} - Y_{\mathrm{calcd}})^2}{(n-p)}\right]^{1/2} \tag{6}$$

where n is the number of experimental points, p is the number of parameters, and Y is the property.

V^E values are negative in all the systems, and deviations in isentropic compressibility and viscosity are negative over the entire range of compositions. The large negative values of V^E and ΔK_s can be ascribed to interaction between π-electrons of the carbonyl group in butyl acetate and π-electrons of the benzene ring in aromatic hydrocarbons. The absolute values of V^E are in the order *o*-xylene < *m*-xylene < *p*-xylene, whereas for ΔK_s the order is *m*-xylene > *p*-xylene > *o*-xylene.

Literature Cited

(1) Hossein, I.; Reddy, K. D.; Rao, M. V. P. *J. Chem. Eng. Data* **1984**, *29*, 474.
(2) Awwad, A. M.; Jbara, K. A.; Dujaili, A. H. A. *Thermochim. Acta* **1988**, *129*, 249.
(3) Ramachandran, D.; Rambabu, K.; Mohan Krishnan, K.; Raman, G. K. *Phys. Chem. Liq.*, in press.
(4) Fermeglia, M.; Lapasin, R. *J. Chem. Eng. Data* **1988**, *33*, 415.
(5) Gowrisankar, M.; Rambabu, K.; Venkateswarlu, P.; Raman, G. K.; *Phys. Chem. Liq.* **1994**, *28*, 29.
(6) Hossein, I. Ph.D. Thesis, Sri Venkateswara University, Tirupati, India, 1984.
(7) Rathnam, M. V. *J. Chem. Eng. Data* **1988**, *33*, 509.
(8) Vogel, A. I. *J. Chem. Soc.* **1948**, 624.
(9) Govindappa, J., Rambabu, K.; Venkateswarlu, P.; Raman, G. K. *Phys. Chem. Liq.* **1988**, *18*, 273.
(10) Riddick, J. A.; Bunger, W. B.; Sakano, J. K. *Organic Solvents, Techniques of Chemistry*, 4th ed.; John Wiley and Sons: New York, 1986; Vol. II.
(11) Timmerman, J. *Physico – Chemical Constants of Pure Organic Compounds*; Elsevier Publication Co.: Amsterdam, 1950, 1962.
(12) Hala, E.; Pick, J.; Fried, V.; Vilivm, O. *Vapor – Liquid Equilibrium*; Pergamon Press: New York, 1967.
(13) Reddy, K. S.; Naidu, P. R. *Can. J. Chem.* **1977**, *76*, 55.
(14) Redlich, O.; Kister, A. T. *Ind. Eng. Chem.* **1948**, *40*, 345.

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