Kanazawa University, for the use of its facilities.

Glossary

a_{ij}	binary interaction parameter, K
P	total pressure, kPa
P_i^s	vapor pressure of pure component i, kPa
q_i	molecular-geometric area parameter for component i
q_i'	molecular-interaction area parameter for component i
r_i	molecular volume parameter for pure component i
R	gas constant, 8.314 J/(mol K)
T	absolute temperature, K
v_i^L	liquid molar volume of pure component i, cm^3/mol
x_i	liquid-phase mole fraction of component i
y_i	vapor-phase mole fraction of component i
Z	lattice coordination number, a constant set equal to 10

Greek Letters

γ_i	activity coefficient of component i
θ_i	area fraction defined by eq 7
θ_i'	area fraction defined by eq 8
Λ_{ij}	Wilson binary parameter
$\Lambda\lambda_{ij}$	Wilson binary interaction parameter, J/mol
Δu_{ij}	UNIQUAC binary interaction parameter, J/mol
σ_F^2	variance of fit
τ_{ij}	UNIQUAC binary parameter
ϕ_i	volume fraction defined by eq 6
ψ_i	fugacity coefficient of component i
ψ_i^s	fugacity coefficient of pure component i at system temperature and P_i^s

Subscript

i	component

Superscript

s	saturation

Registry No. Acetonitrile, 75-05-8; 2-butanone, 78-93-3; benzene, 71-43-2; methanol, 67-56-1.

Literature Cited

(1) Ohta, T.; Koyabu, J.; Nagata, I. *Fluid Phase Equilib.* **1981**, *7*, 65-73.

(2) Dohnal, V.; Blahova, D.; Holub, R. *Fluid Phase Equilib.* **1982**, *9*, 187-200.

(3) Kraus, J.; Linek, J. *Collect. Czech. Chem. Commun.* **1971**, *36*, 2547-67.

(4) Zharov, V. T.; Malegina, N. D.; Morachevsky, A. G. *Zh. Prikl. Khim.* **1965**, *38*, 2132-4.

(5) Brown, I.; Smith, F. *Aust. J. Chem.* **1955**, *8*, 62-7.

(6) Palmer, D. A.; Smith, B. D. *J. Chem. Eng. Data* **1972**, *17*, 71-6.

(7) Werner, G.; Schuberth, H. *J. Prakt. Chem.* **1966**, *31*, 225-336.

(8) Nagata, I.; Katoh, K.; Koyabu, J. *Thermochim. Acta* **1981**, *47*, 225-33.

(9) Scatchard, G.; Wood, S. E.; Mochel, J. M. *J. Am. Chem. Soc.* **1946**, *68*, 1957-60.

(10) Prausnitz, J. M.; Anderson, T. F.; Grens, E. A.; Eckert, C. A.; Hsieh, R.; O'Connell, J. P. "Computer Calculations for Multicomponent Vapor-Liquid and Liquid-Liquid Equilibria"; Prentice-Hall: Englewood Cliffs, NJ, 1980; Chapters 3 and 4, Appendix D.

(11) Fredenslund, A.; Gmehling, J.; Rasmussen, P. "Vapor-Liquid Equilibria Using UNIFAC"; Elsevier: Amsterdam, 1977; Chapter 5.

(12) Gmehling, J.; Rasmussen, P.; Fredenslund, A. *Ind. Eng. Chem. Process Des. Dev.* **1982**, *21*, 118-27.

(13) Skjold-Jørgensen, S.; Kolbe, B.; Gmehling, J.; Rasmussen, P. *Ind. Eng. Chem. Process Des. Dev.* **1979**, *18*, 714-22.

(14) Boublik, T.; Benson, G. C. *Can. J. Chem.* **1969**, *47*, 539-42.

(15) Hayden, J. G.; O'Connell, J. P. *Ind. Eng. Chem. Process Des. Dev.* **1975**, *14*, 209-16.

(16) Spencer, C. F.; Danner, R. P. *J. Chem. Eng. Data* **1972**, *17*, 236-41.

(17) Anderson, T. F.; Prausnitz, J. M. *Ind. Eng. Chem. Process Des. Dev.* **1978**, *17*, 552-61.

(18) Christiansen, L. J.; Fredenslund, A. *AIChE J.* **1975**, *21*, 49-57.

(19) Gmehling, J.; Onken, U. "Vapor-Liquid Equilibrium Data Collection"; DECHEMA: Frankfurt/Main, 1977; Vol. I, Part 1.

(20) Gmehling, J.; Onken, U. "Vapor-Liquid Equilibrium Data Collection"; DECHEMA: Frankfurt/Main, 1977; Vol. I, Part 2a.

(21) Gmehling, J.; Onken, U.; Arlt, W. "Vapor-Liquid Equilibrium Data Collection"; DECHEMA: Frankfurt/Main, 1978; Vol. I, Part 2b.

(22) Gmehling, J.; Onken, U.; Arlt, W. "Vapor-Liquid Equilibrium Data Collection"; DECHEMA: Frankfurt/Main, 1979; Vol. I, Parts 3 and 4, pp 285-7, 293.

(23) Gmehling, J.; Onken, U.; Arlt, W. "Vapor-Liquid Equilibrium Data Collection"; DECHEMA: Frankfurt/Main, 1980; Vol. I, Part 6a.

(24) Gmehling, J.; Onken, U.; Arlt, W. "Vapor-Liquid Equilibrium Data Collection"; DECHEMA: Frankfurt/Main, 1980; Vol. I, Part 6b.

(25) Gmehling, J.; Onken, U.; Arlt, W. "Vapor-Liquid Equilibrium Data Collection"; DECHEMA: Frankfurt/Main, 1980; Vol. I, Part 7, pp 122, 126, 131.

(26) Gmehling, J.; Onken, U.; Arlt, W. "Vapor-Liquid Equilibrium Data Collection"; DECHEMA: Frankfurt/Main, 1980; Vol. I, Part 1a.

(27) Gmehling, J.; Onken, U.; Arlt, W. "Vapor-Liquid Equilibrium Data Collection"; DECHEMA: Frankfurt/Main, 1982; Vol. I, Part 2c.

(28) Riddick, J. A.; Bunger, W. B. "Organic Solvents", 3rd ed.; Wiley-Interscience: New York, 1970; pp 107, 145, 243, 399.

(29) Brown, I.; Smith, F. *Aust. J. Chem.* **1954**, *7*, 269-72.

Received for review July 2, 1982. Revised manuscript received January 3, 1983. Accepted April 9, 1983.

Ultrasonic Velocity in Binary Mixtures of Alkylbenzenes at 25 °C

G. Vitali* and G. Gioia Lobbia

Dipartimento di Scienze Chimiche, Università degli Studi, 62032 Camerino, Italy

Density and ultrasonic velocity values in the frequency range 2.5-15 MHz at 25 °C were measured for binary mixtures of ethylbenzene, *o*-xylene, *m*-xylene, and *p*-xylene. Our data were discussed and compared, where possible, with those found in the literature.

Introduction

Ultrasonic velocity data are of increasing interest in physical chemistry because, as described in the literature (*1-7*), they are the basis of structural studies of liquids. In fact, quantities such as internal pressure and adiabatic compressibility depend on the liquid structure, the extent of molecular interaction (*8*), and the intermolecular free path (*5*) and they may be calculated by using ultrasonic velocity data (*9*). Compressibility is one of the fundamental measurements for calculating reduction parameters in the state equation according to Flory statistics (*1*, *7*, *10*, *11*). In the course of physicochemical investigations of organic systems being carried out in this department (*1*, *12*, *13*), we measured the ultrasonic velocities of mixtures of alkylbenzenes, for use in successive physicochemical studies.

Experimental Section

The interferometric method employed for the measurement of ultrasonic velocity is described elsewhere (*3*, *4*). The

0021-9568/83/1728-0402$01.50/0

Table I. Values of *U* (m s^{-1}) as a Function of the Mole Fraction X_1

ethylbenzene (1)-*o*-xylene (2)		ethylbenzene (1)-*m*-xylene (2)		ethylbenzene (1)-*p*-xylene (2)	
X_1	U	X_1	U	X_1	U
1.0000	1297	1.0000	1297	1.0000	1297
0.8927	1299	0.8945	1298	0.8946	1296
0.7979	1301	0.8006	1297	0.8017	1292
0.6916	1305	0.6960	1299	0.7062	1290
0.5971	1306	0.6007	1298	0.6010	1291
0.4968	1307	0.5069	1297	0.5084	1289
0.3971	1312	0.4010	1298	0.4019	1288
0.2921	1317	0.2959	1299	0.2976	1287
0.1978	1322	0.2002	1299	0.2012	1289
0.0932	1324	0.0970	1298	0.0979	1289
0.0000	1328	0.0000	1300	0.0000	1290

Table II. Values of *U* (m s^{-1}) as a Function of the Mole Fraction X_1

o-xylene (1)-*m*-xylene (2)		*o*-xylene (1)-*p*-xylene (2)		*m*-xylene (1)-*p*-xylene (2)	
X_1	U	X_1	U	X_1	U
1.0000	1328	1.0000	1328	1.0000	1300
0.8965	1325	0.8958	1324	0.8938	1297
0.8027	1322	0.8028	1319	0.8003	1294
0.7077	1319	0.7088	1321	0.7048	1296
0.6038	1315	0.6050	1314	0.6014	1294
0.5100	1313	0.5116	1307	0.5073	1295
0.4034	1307	0.4051	1303	0.4010	1290
0.2997	1304	0.3004	1299	0.2962	1287
0.2026	1303	0.2031	1295	0.2003	1288
0.0989	1299	0.0992	1291	0.0972	1289
0.0000	1300	0.0000	1290	0.0000	1290

Table III. Values of Density (g mL^{-1}) as a Function of the Mole Fraction X_1

ethylbenzene (1)-*o*-xylene (2)		ethylbenzene (1)-*m*-xylene (2)		ethylbenzene (1)-*p*-xylene (2)	
X_1	d	X_1	d	X_1	d
1.0000	0.8630	1.0000	0.8630	1.0000	0.8630
0.8927	0.8645	0.8945	0.8626	0.8946	0.8625
0.7979	0.8653	0.8006	0.8621	0.8017	0.8618
0.6916	0.8665	0.6960	0.8617	0.7062	0.8613
0.5971	0.8677	0.6007	0.8613	0.6010	0.8604
0.4968	0.8688	0.5069	0.8609	0.5084	0.8599
0.3971	0.8700	0.4010	0.8605	0.4019	0.8591
0.2921	0.8713	0.2959	0.8602	0.2976	0.8584
0.1978	0.8726	0.2002	0.8600	0.2012	0.8577
0.0932	0.8739	0.0970	0.8596	0.0979	0.8570
0.0000	0.8751	0.0000	0.8596	0.0000	0.8564

Table IV. Values of Density (g mL^{-1}) as a Function of the Mole Fraction X_1

o-xylene (1)-*m*-xylene (2)		*o*-xylene (1)-*p*-xylene (2)		*m*-xylene (1)-*p*-xylene (2)	
X_1	d	X_1	d	X_1	d
1.0000	0.8751	1.0000	0.8751	1.0000	0.8596
0.8965	0.8735	0.8958	0.8732	0.9838	0.8591
0.8027	0.8719	0.8028	0.8713	0.8003	0.8589
0.7077	0.8704	0.7088	0.8695	0.7048	0.8587
0.6038	0.8689	0.6050	0.8677	0.6014	0.8583
0.5100	0.8674	0.5116	0.8659	0.5073	0.8580
0.4034	0.8658	0.4051	0.8639	0.4010	0.8578
0.2997	0.8641	0.3004	0.8621	0.2962	0.8574
0.2026	0.8627	0.2031	0.8601	0.2003	0.8571
0.0989	0.8611	0.0992	0.8582	0.0972	0.8567
0.0000	0.8596	0.0000	0.8564	0.0000	0.8564

equipment was built in the "Instytut of Fundamental Thecnological Research" of the Polish Academy of Sciences (Warsaw). The Fluka puriss. p.a. products were used without further purification; the purity was guaranteed to be >99.0%.

Temperature control within 0.1 °C was obtained by means of a Lauda ultrathermostat, for velocity measurements.

The mixtures were prepared as w/w solutions. The ultrasonic equipment can be used in the frequency range 2.5–15 MHz and in this range, within the experimental precision reported (*3*) (1 m s^{-1}), relaxation phenomena are not observed. This has also been reported by Linde (*14*) for the whole ultrasonic range. Probably a relaxation phenomenon exists in the hypersonic range (*15*, *16*).

Results and Discussion

The ultrasonic velocities at 25 °C, as a function of mole fraction, are given in Tables I and II. These results are independent of the frequency within the range 2.5–15 MHz. In Tables III and IV the density values at 25 °C of the different

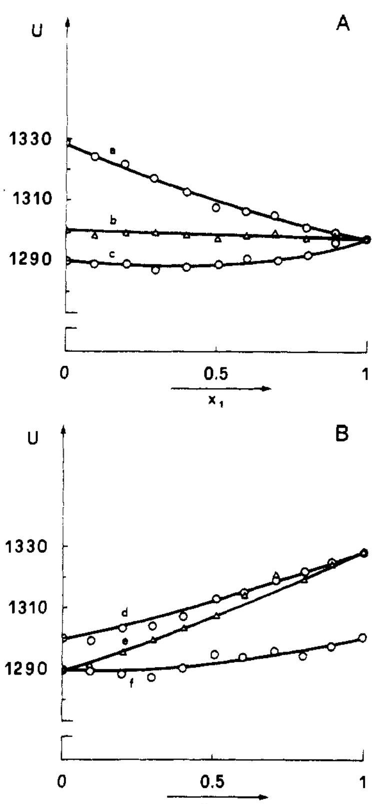

Figure 1. Ultrasonic velocity vs. the mole fraction X_1: (a) ethylbenzene (1)–*o*-xylene (2), (b) ethylbenzene (1)–*m*-xylene (2), (c) ethylbenzene (1)–*p*-xylene (2), (d) *o*-xylene (1)–*m*-xylene (2), (e) *o*-xylene (1)–*p*-xylene (2), (f) *m*-xylene (1)–*p*-xylene (2).

mixtures are given; they were obtained by a conventional pycnometric technique. A reliability of $\pm 1 \times 10^{-4}$ g mL^{-1} was obtained. The adiabatic compressibility (β_s), ultrasonic velocity (U), and density (d) are related by the equation (*9*)

$$\beta_s = (U^2 d)^{-1} \qquad (1)$$

The data in Tables I–IV allow us to evaluate the adiabatic compressibility. The trend of ultrasonic velocity and compressibility, as a function of the mixture composition, is shown in Figures 1 and 2. Padmini et al. (*17*) calculated a molar sound velocity, R, of 1348 and 1351 m s^{-1} for ethylbenzene and *o*-xylene, respectively. From these data it is possible to derive velocities of $1315._5$ and $1380._8$ m s^{-1}, by using our density data at 25 °C. Nath et al. (*8*) gave a value of 1288.8 m s^{-1} for the *p*-xylene at 30 °C. Reddy et al. (*6*) give 1335 m s^{-1} for *o*-xylene at 29.4 °C, 1308 m s^{-1} for *m*-xylene at 28 °C, and 1310 m s^{-1} for *p*-xylene at 29.5 °C. Prasad (*5*) gives 1367 m s^{-1} for *o*-xylene at 23 °C. Takagi (*18*) gives 1292.5 m s^{-1} at 30 °C and 0.1 MPa for the *p*-xylene, and 1303.8 m s^{-1} at 30 °C and 0.1 MPa for the *m*-xylene. Because of the differences in the experimental conditions, a rigorous comparison between literature and experimental results cannot be made, but in general it is possible to note a fairly good agreement.

We have not found any data for mixtures containing the isomers of alkylbenzenes as used by us. The trend U (ultrasonic velocity) vs. X (mole fraction) is linear, within the experimental sensitivity, for the ethylbenzene–*m*-xylene, *o*-xylene–*m*-xylene, *o*-xylene–*p*-xylene mixtures, while the ethylbenzene–*o*-xylene, ethylbenzene–*p*-xylene, *m*-xylene–*p*-xylene systems show a negative deviation from the additive rule, more pronounced in the ethylbenzene–*p*-xylene system. Obviously analogous behavior, that is, positive deviations, exists for the compressibility. In order to elucidate this trend the research needs to be continued, especially with the application of Flory statistics, and therefore the expansion coefficient, α, must be measured.

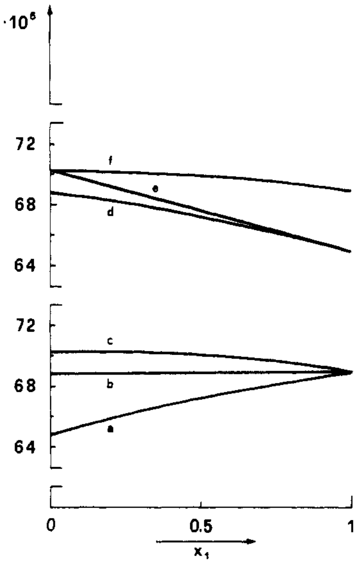

Figure 2. Adiabatic compressibility vs. the mole fraction X_1: (a) ethylbenzene (1)–*o*-xylene (2), (b) ethylbenzene (1)–*m*-xylene (2), (c) ethylbenzene (1)–*p*-xylene (2), (d) *o*-xylene (1)–*m*-xylene (2), (e) *o*-xylene (1)–*p*-xylene (2), (f) *m*-xylene (1)–*p*-xylene (2).

Acknowledgment

We thank V. Amici for technical assistance.

Registry No. Ethylbenzene, 100-41-4; *o*-xylene, 95-47-6; *m*-xylene, 108-38-3; *p*-xylene, 106-42-3.

Literature Cited

(1) Vitali, G.; Berchiesi, G.; Gioia Lobbia, G.; Fanelli, E. *J. Chem. Res., Miniprint* **1981**, 8382–90.
(2) Vitali, G.; Berchiesi, G.; Berchiesi, M. A.; Gioia Lobbia, G. *J. Chim. Phys. Phys.-Chim. Biol.* **1980**, *77*, 865–8.
(3) Berchiesi, G.; Berchiesi, M. A.; Vitali, G.; Valenti, V. *Can. J. Chem.* **1979**, *57*, 2010–2.
(4) Vitali, G.; Berchiesi, G.; Berchiesi, M. A.; Valenti, V. *Gazz. Chim. Ital.* **1979**, *109*, 291.
(5) Prasad, N.; Prakash, S. *J. Chem. Eng. Data* **1977**, *22*, 49–50.
(6) Reddy, K. C.; Subrahmanyam, S. V.; Bhimasenachar, J. *J. Trans. Faraday Soc.* **1962**, *58*, 2352–7.
(7) Reddy, K. S.; Sreenivasulu, M.; Naidu, P. R. *Z. Phys. Chem.* **1981**, *124*, 149–54.
(8) Nath, J.; Dubey, S. N. *J. Phys. Chem.* **1980**, *84*, 2166–70.
(9) Blandamer, M. J. "Introduction to Chemical Ultrasonics"; Academic Press: London, 1973; p 12.
(10) Flory, P. J. *J. Am. Chem. Soc.* **1965**, *87*, 1833–8.
(11) Abe, A.; Flory, P. J. *J. Am. Chem. Soc.* **1965**, *87*, 1838–46.
(12) Gioia Lobbia, G.; Vitali, G.; Berchiesi, M. A.; Berchiesi, G. *Ber. Bunsenges. Phys. Chem.* **1981**, *85*, 628–31.
(13) Gioia Lobbia, G.; Vitali, G.; Berchiesi, G. *Thermochim. Acta* **1982**, *57*, 5–11.
(14) Linde, B.; Sliwinski, A. *Acoust. Lett.* **1978**, *2*, 65–8.
(15) Zinov'ev, O. I.; Shakhparonov, M. I.; Parzyan, V. A.; Prikhod'ko, A. Ya.; Karshibaev, A. K. *Chem. Abstr.* **1976**, *84*, 95865*g*.
(16) Sukhotina, G. G.; Shakhparonov, M. I. *Chem. Abstr.* **1966**, *65*, 3028*c*.
(17) Padmini, P. R. K.; Subba Rao, K.; Ramanchandra Rao, B. *Trans. Faraday Soc.* **1960**, *56*, 1404–8.
(18) Takagi, T. *J. Chem. Thermodyn.* **1981**, *13*, 291–9.

Received for review November 8, 1982. Revised manuscript received April 4, 1983. Accepted April 29, 1983. Thanks are due to C.N.R. of Rome for finanical support.