difference in the number of hydrogen atoms in the compound formula and partly to inaccurate estimation of the difference between ΔH_f° for $TiH_{2.00}$ and that for $TiH_{1.73}$ in the JANAF tables.

Literature Cited

(1) A. Sieverts and A. Gotta, *Z. Anorg. Allg. Chem.*, **199**, 384 (1931).
(2) B. Stalinski and Z. Bieganski, *Bull. Acad. Pol. Sci., Ser. Sci. Chim.*, **8**, 243 (1960).
(3) B. Stalinski and Z. Bieganski, *Bull. Acad. Pol. Sci., Ser. Sci. Chim.*, **10**, 247 (1962).
(4) T. R. P. Gibb, Jr., J. J. McSharry, and R. W. Bragdon, *J. Am. Chem. Soc.*, **73**, 1754 (1951).
(5) R. M. Haag and F. J. Shipko, *J. Am. Chem. Soc.*, **78**, 5155 (1956).
(6) A. D. McQuillan, *Proc. R. Soc. London., Ser. A*, **204**, 309 (1950).
(7) D. R. Stull and H. Prophet, *Natl. Stand. Ref. Data Ser., Natl. Bur. Stand.*, **No. 37** (1971).

Received for review July 31, 1978. Accepted July 23, 1979.

Ultrasound Study of Binary Mixtures of Acetone with Ethylene Glycol, Benzene, and Toluene

S. Singh, K. Sivanarayana, R. Kushwaha, and S. Prakash*
Chemical Laboratories, University of Allahabad, Allahabad 211 002, India

Ultrasonic velocity, density, isentropic compressibility, and molecular association have been determined for binary liquid mixtures of acetone with ethylene glycol (I), benzene (II), and toluene (III) at different compositions. The temperatures of study were 23 °C in the former and 27 °C in the latter two. Excess density values are positive in each case. Excess compressibility is negative, except in the case of acetone and ethylene glycol in which it is negative in a mixture rich in ethylene glycol but becomes positive at compositions quite rich in acetone. Excess properties have been used to discuss the molecular interaction taking place between the components of mixtures. The associating nature of ethylene glycol leads to a stronger interaction in I while π electrons of aromatic rings are possibly involved in the interaction in II and III.

An ultrasound study of binary liquid–liquid mixtures has been made by some workers (*9–11*). The nonlinear behavior of ultrasound velocities and isentropic compressibilities with changing mole fractions are attributed to the difference in size of the molecule and the strength of interaction. Lagemann and Corry (*4*) discussed sound property as bond property while Fort and Moore (*3*) have compared the excess compressibility with excess volume. Prakash et al. (*5*) and Bhatgadde and Deshpande (*2*) discussed molecular interaction on the basis of excess free volume. This paper deals with the results obtained from the study of binary liquid mixtures acetone + ethylene glycol (I), acetone + benzene (II), and acetone + toluene (III) with regards to the ultrasound velocity, density, isentropic compressibility, and molecular association. Excess values of density and compressibility also have been reported.

Experimental Section

Materials. All chemicals used were AR (BDH) grade and were redistilled and further purified by standard methods described by Weissberger (*12*). The calculated volumes of liquids were added to one another to get mixtures of different known compositions. The mixtures were kept for 2 h and then they were used for velocity measurements. Water at fixed temperature was circulated around the ultrasound cell for maintaining the temperature within ±0.05 °C during the experiment.

Sound Velocity Measurements. The ultrasound velocities were measured at 5 MHz by using the Debye–Sears (*1*) light diffraction method. The details of instrumental technique have been described previously (*6*). The maximum uncertainty in the velocity measurements was ±0.18%. The maximum error in the compressibility values is ±0.4% and the error in mole fraction is not more than 0.05%.

Density Measurements. The densities of pure liquids and liquid mixtures were determined in a 10-mL calibrated density bottle. To avoid temperature variation, we kept the solution bottles in a container with a thermostat maintaining constant temperature through an electric relay system. The densities were reproducible to 1 part in 10^4.

Results and Calculations

For any homogeneous nondissipative liquid system, the velocity (v) for the compressed acoustic wave is related to the density (ρ) and isentropic compressibility (β_s) of the medium by the well-known equation

$$v = (\rho\beta_s)^{-1/2} \tag{1}$$

Molecular association was determined by Prakash et al. (*7*) by using the expression

$$\text{molecular assocn} = [(v^2_{\text{exptl}}/v^2_{\text{calcd}}) - 1] \tag{2}$$

where v_{calcd}, velocity in the mixture, is given by

$$\left(\frac{1}{x_1M_1 + x_2M_2}\right)\frac{1}{v^2_{\text{calcd}}} = \left(\frac{x_1}{M_1v_1^2} + \frac{x_2}{M_2v_2^2}\right) \tag{3}$$

where x_1 and M_1 are mole fraction and molecular weight, respectively, for acetone and x_2 and M_2 are the same properties for the second component of the mixtures.

The excess properties are given by the relation

$$A^E = A_{\text{exptl}} - A_{\text{id}} \tag{4}$$

where $A_{\text{id}} = (x_1A_1 + x_2A_2)$ and A^E represents the excess property under consideration.

The mole fractions, ultrasound velocities, densities, isentropic compressibilities, molecular association, and excess values of compressibilities and densities are listed in Table I. Each set of results was fitted with a Redlich–Kister (*8*) form of the type

$$A^E = x(1 - x)\sum_{j=1}^{n} a_j(1 - 2x)^{j-1} \tag{5}$$

where a_j = polynomial coefficients and n = polynomial degree.

0021-9568/79/1724-0279$01.00/0 © 1979 American Chemical Society

Table I

mole fraction of acetone	ν, m/s	ρ, g/mL	$10^{12} \times \beta_s$, cm²/dyn	molecular assocn	$10^{12}\beta_s^E$, cm²/dyn	ρ^E, g/mL
(I) Acetone + Ethylene Glycol, 23 °C						
0.0000	1721	1.1034	30.60	0.0000	0.00	0.0000
2.2139	1632	1.0705	35.07	+0.1126	−7.74	+0.0343
0.3180	1560	1.0401	39.51	+0.1098	−9.25	+0.0367
0.5211	1450	0.9841	48.33	+0.1121	−12.03	+0.0445
0.6201	1375	0.9404	56.24	+0.0657	−9.77	+0.0319
0.7174	1270	0.9064	68.40	−0.0367	−3.17	+0.0285
0.8132	1210	0.8697	78.53	−0.0779	+1.49	+0.0219
1.0000	1202	0.7891	87.71	0.0000	0.00	0.0000
(II) Acetone + Benzene 27 °C						
0.0000	1292	0.8715	68.74	0.0000	0.00	0.0000
0.2321	1265	0.8535	73.22	+0.0426	−1.66	+0.0025
0.3424	1253	0.8471	75.19	+0.0556	−2.58	+0.0056
0.4464	1241	0.8399	77.49	+0.0629	−3.05	+0.0058
0.5474	1230	0.8279	79.65	+0.0666	−3.56	+0.0067
0.7784	1205	0.8086	85.17	+0.0562	−3.09	+0.0022
0.8287	1187	0.8010	88.61	+0.0361	−2.04	+0.0026
1.0000	1158	0.7835	95.18	0.0000	0.00	0.0000
(III) Acetone + Toluene 27 °C						
0.0000	1308	0.8606	67.92	0.0000	0.00	0.0000
0.2653	1269	0.8482	73.21	+0.0793	−1.94	+0.0082
0.3823	1272	0.8443	73.20	+0.1299	−5.14	+0.0133
0.4905	1256	0.8361	75.32	+0.1344	−5.47	+0.0134
0.5909	1227	0.8257	80.44	+0.1043	−3.59	+0.0108
0.6843	1217	0.8165	82.69	+0.0998	−3.88	+0.0088
0.8524	1187	0.8021	88.48	+0.0564	−2.67	+0.0073
1.0000	1158	0.7835	95.18	0.0000	0.00	0.0000

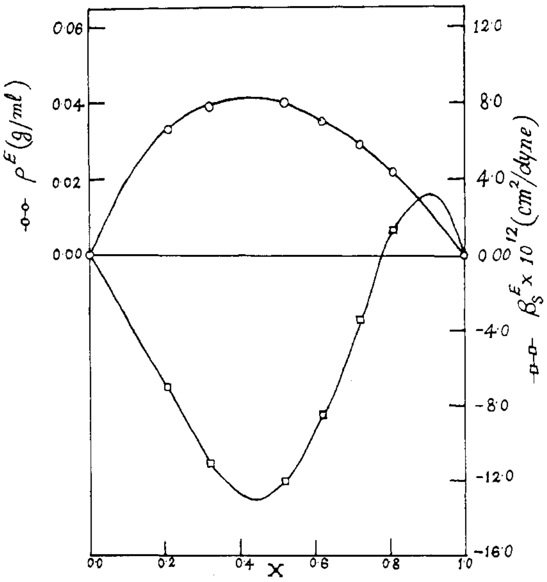

Figure 1. Variation in excess compressibility (β_s^E) and density (ρ^E) of the system acetone + ethylene glycol for different mole fractions of acetone (x) at 23 °C.

The method of least squares was used to determine the values of the coefficients a_j. In each case the optimum number of coefficients was ascertained from an examination of the variation of the standard error of estimate within

$$\sigma_x = [\sum(A^E_{\text{exptl}} - A^E_{\text{calcd}})^2/(n_{\text{obsd}} - n)]^{1/2} \qquad (6)$$

where n_{obsd} is the number of measurements. The values for the coefficients a_j and the estimate of the standard error σ_x, eq 6 are summarized in Table II. Figures 1, 2, and 3 show the experimental values obtained for the excess property under consideration. The continuous curves for β_s^E and ρ^E in Figures 1, 2, and 3 were calculated by making use of the coefficients obtained from eq 5.

Table II

system	function	a_1	a_2	a_3	σ_x
(I) acetone + ethylene glycol	β_s^E	−49.732	−36.323	90.277	1.401
	ρ^E	0.1593	0.0478	0.0307	0.004
(II) acetone + benzene	β_s^E	−12.322	4.455	−4.670	0.388
	ρ^E	0.2205	0.0018	−0.0099	0.001
(III) acetone + toluene	β_s^E	−17.559	5.968	0.941	1.264
	ρ^E	0.0488	−0.0035	0.0008	0.002

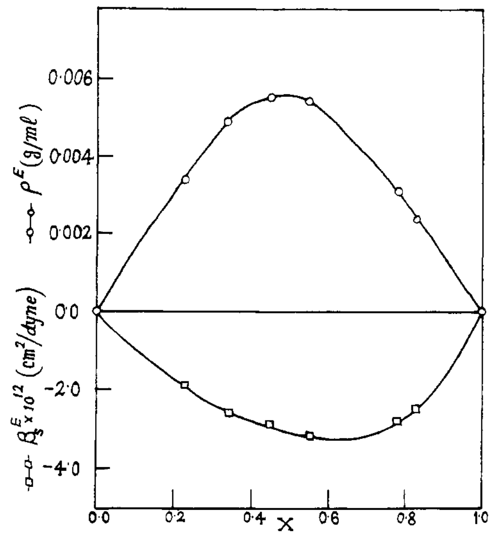

Figure 2. Variation in excess compressibility (β_s^E) and density (ρ^E) of the system acetone + benzene for different mole fractions of acetone (x) at 27 °C.

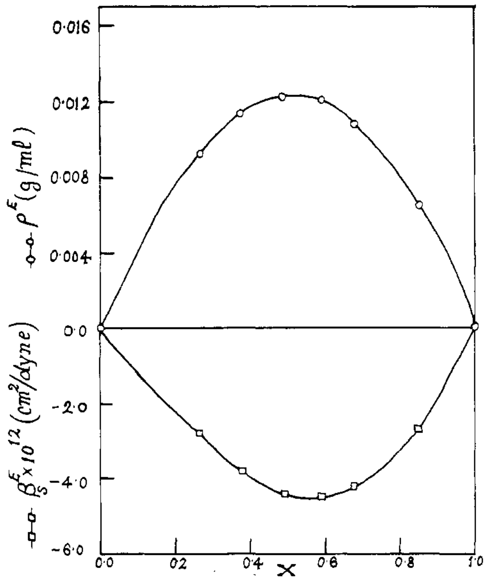

Figure 3. Variation in excess compressibility (β_s^E) and density (ρ^E) of the system acetone + toluene for different mole fractions of acetone (x) at 27 °C.

Discussion

A positive excess value of compressibility is indicative of relatively weak interaction, as is also the case with excess enthalpy, heat of mixing, and entropy of liquid mixtures. ρ^E is positive in all three cases while β_s^E is found to be negative in II and III. In the case of acetone + ethylene glycol, β_s^E changes sign to become positive at composition very rich in acetone. β_s^E has quite significant values. For system I, β_s^E is unexpectedly high, perhaps due to much difference in velocity and density of acetone and ethylene glycol. Molecular associations have been found to be positive. In case I it becomes negative at higher mole fraction of acetone. Molecular associations have been found to be positive in II and III.

Acetone has been mixed with nonpolar benzene, nearly nonpolar toluene, and associating ethylene glycol. Negative excess compressibilities are shown by the systems involving hydrogen bonding, these being large in those cases where one component is associated in the pure state (*3*). Acetone + ethylene glycol forms such a system and large negative values of excess compressibility have been recorded in this case which is indicative of strong interaction between the components of this mixture. The positive portion of the smooth curve of β_s^E shows a maximum at 0.9 mole fraction of acetone (Figure 1). Negative excess compressibilities have been observed for acetone + benzene (Figure 2) and acetone + toluene (Figure 3). Both benzene and toluene are nonpolar but their polarizability is high. The interaction in these cases seems to involve the π electrons on the aromatic rings.

Glossary

v	ultrasound velocity, m s^{-1}
β_s	isentropic compressibility, cm^2 dyn^{-1}
ρ	density, g mL^{-1}
σ_x	standard deviation
n	polynomial degree

Subscripts

E	excess function
calcd	calculated value
id	ideal value
exptl	experimental value
obsd	observed value

Literature Cited

(1) Debye, P., Sears, F. W., *Proc. Natl. Acad. Sci. U.S.A.*, **18**, 410 (1932).
(2) Deshpande, D. D., Bhatgadde, L. G., *J. Phys. Chem.*, **72**, 261 (1968); *J. Chem. Eng. Data*, **16**, 469 (1971).
(3) Fort, R. J., Moore, W. R., *Trans. Faraday Soc.*, **61**, 2102 (1965).
(4) Lagemann, R. T., Corry, J. E., *J. Chem. Phys.*, **10**, 759 (1942).
(5) Prakash, S., Prasad, N., Prakash, O., *Indian J. Phys.*, **50**, 801 (1976).
(6) Prasad, N., Prakash, S., *J. Chem. Eng. Data*, **22**, 49 (1977).
(7) Prasad, N., Prakash, O., Singh, S., Prakash, S., *Ultrasonics*, **16**, 77 (1978).
(8) Redlich, O., Kister, A. T., *Ind. Eng. Chem.*, **40**, 345 (1948).
(9) Snyder, W. J., Snyder, J. R., *J. Chem. Eng. Data*, **19**, 270 (1974).
(10) Tuomikoski, P., Nurmi, P., *Comments Phys. Math.* 10, 11 (1940).
(11) Vilcu. R., Simion, A., *Rev. Roum Chim.*, **21**, 177 (1976).
(12) Weissberger, A., "Techniques of Organic Chemistry", Vol. 7, Interscience, New York, 1959, pp 315, 318, 362, 379.

Received for review October 26, 1978. Accepted July 30, 1979. Financial assistance from SCST (Lucknow) and UGC (Delhi) is gratefully acknowledged.

Thermal Conductivity of Gaseous Mixtures of Methane with Nitrogen and Carbon Dioxide

Peter L. Christensen and Aage Fredenslund*
Instituttet for Kemiteknik, Danmarks Tekniske Højskole, DK-2800 Lyngby, Denmark

Thermal conductivities of nearly equimolar, gaseous mixtures of methane with carbon dioxide and nitrogen are measured by using a coaxial cylinder conductivity cell. Results obtained in the same apparatus for pure methane are within 3% of the thermal conductivities predicted by using the correlation of Hanley et al.

Introduction

Knowledge of the thermal conductivities of natural gases and related mixtures is of central importance in the design of natural gas liquefaction plants and related processes. Several models have been proposed for the estimation of mixture thermal conductivities from pure-component conductivities only; see, for example, ref 1, Chapter 10. Due to the scarcity of experimental data, however, these models cannot be fully verified. In this work we report thermal conductivities of the gaseous mixtures methane–carbon dioxide and methane–nitrogen. These measurements supplement the results reported by Rosenbaum (*2*) for methane–carbon dioxide, which contain data at temperatures higher than those of this work. To our knowledge, thermal conductivities of the mixture methane–nitrogen have not been reported previously.

Thermal Conductivity Cell

The coaxial cylinder conductivity cell is constructed according to the principles given by Guildner (*3*). A schematic diagram of the cell is shown in Figure 1. The cell is constructed from silver, and Pyrex sphere and aluminum holders are dimensioned such that their collective thermal expansion coefficient equals that of silver. The dimensions of the cell are as follows: emitter diameter = 14.98 ± 0.01 mm; emitter length = 83.59 ± 0.01 mm; conductivity gap = 0.52 ± 0.01 mm.

Experimental Section

The thermal conductivity cell is placed in the air thermostat described in ref 4. The cell is contained within a high-pressure steel cylinder. During operation, the space between the cell and the cylinder is occupied by the gas under investigation. The temperature of the air in the thermostat is maintained within 0.01 K of the desired temperature. When the resistances of the three thermistors have remained constant for at least 60 min, the values of the resistances are recorded and the voltage to the heaters in the emitter and heat guard is switched on. The electrical energy supplied to the two heaters is regulated such that the temperature rise in the emitter and heat guard becomes nearly equal. The difference between the emitter and heat guard temperature rise is calculated from

$$D_1 = T(\mathrm{R3}) - T(\mathrm{R03}) - [T(\mathrm{R1}) - T(\mathrm{R01})] \tag{1}$$

$T(\mathrm{R})$ is an analytical expression giving the temperature as a function of the thermistor resistance; the function, based on standards supplied by the manufacturer, has the form of a polynomial. This approach is reasonable as long as the differences $[T(\mathrm{R3})-T(\mathrm{R03})$ and $T(\mathrm{R1})-T(\mathrm{R01})]$ are small. (R01 = resistance of thermistor 1 before heating, R03 = resistance of thermistor 3 before heating, R1 = resistance of thermistor

0021-9568/79/1724-0281$01.00/0 © 1979 American Chemical Society