

Excess Molar Gibbs Free Energies and Isentropic Compressibilities of 1,2-Dibromoethane + Cyclohexane or Tetrachloromethane

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Excess molar Gibbs free energies (G^E) and ultrasonic speeds for 1,2-dibromoethane (1) + cyclohexane (2) or tetrachloromethane (2) over the whole composition range have been measured experimentally at 298.15 K. The values of isentropic compressibility (K_s) and excess isentropic compressibility (K_s^E) have been evaluated from ultrasonic speeds, and excess Gibbs free energies are calculated for the vapor pressure by using Barker's method.

Introduction

Two conformational isomers (gauche and trans) of 1,2-dibromoethane (DBE) are known (1, 2) to be in equilibrium at room temperature. It has been shown that the gauche isomer becomes destabilized (3, 4) in nonpolar solvents, resulting in the loss of favorable orientation. Excess thermodynamic functions are known (5-14) to exist as a result of interactions taking place between the two components of the binary mixtures. In the present investigations, excess molar Gibbs free energies and ultrasonic speeds for DBE (1) + cyclohexane (2) and DBE (1) + tetrachloromethane (2) have been obtained for the whole composition range. The values of isentropic (K_s) and excess isentropic (K_s^E) compressibilities have been evaluated. The values of G^E , K_s , and K_s^E have also been estimated using Flory's theory (15, 16).

Experimental Section

1,2-Dibromoethane, cyclohexane, and tetrachloromethane (BDH, AR grade) were purified by standard procedures (17). The purities of the final samples were checked with density measurements at 298.15 ± 0.01 K. The experimental values agreed with the literature values (18, 19) within ± 0.05 kg m⁻³. Total vapor pressures of DBE (1) + cyclohexane (2) and DBE (1) + tetrachloromethane (2) were measured as a function of liquid-phase mole fraction of DBE at a constant temperature by using a static method in the manner described in the literature (20). In the static vapor pressure measurement, mixtures of degassed liquids of known compositions were introduced into a glass vessel containing a coaxial cylindrical copper cell attached to a manometer, both being immersed in a water thermostat controlled to ± 0.01 K by a toluene regulator. Vapor pressures were measured with a cathetometer, which could read with an accuracy of up to ± 0.001 cm. All vapor pressure measurements were reproducible to better than ± 0.005 kPa. Our experimental values for the vapor pressure of DBE, cyclohexane, and tetrachloromethane compared well (to within $\pm 0.3\%$) with the corresponding computed literature values (18, 21). The composition of the mixture in the liquid phase was determined by using a capacitance measurement of a cell (fitted into the vapor pressure still) using a dipolemeter (type RL 09, S&I Instruments, India). The uncertainty in the liquid-phase composition was 0.01%. The uncertainty in G^E , if expressed as the uncertainty of total pressure, corresponds roughly to 0.1 kPa. Ultrasonic speeds at a frequency of 2 MHz were determined using a quartz crystal interferometer (Mittal Enterprises, New Delhi, India). The quartz crystal was fitted at the bottom of the measuring cell to produce waves of known frequency.

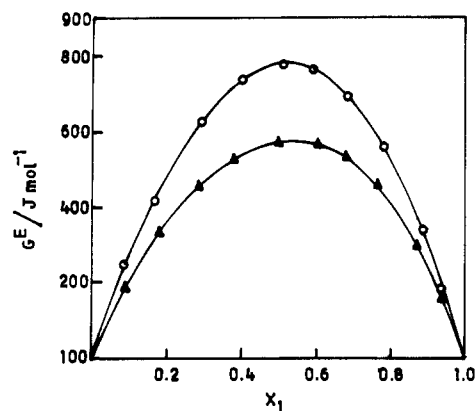


Figure 1. Excess molar Gibbs free energies G^E at 298.15 K for (O) DBE (1) + cyclohexane (2) and (▲) DBE (1) + tetrachloromethane (2).

The measuring cell was a specially designed double-walled cell in which water was circulated to keep the temperature constant (298.15 ± 0.1 K). The uncertainty in the speed of sound measurement was $\pm 0.03\%$. There is good agreement between the experimentally observed and literature values (19, 23, 24) of ultrasonic speeds (Table 1).

Results

Molar Gibbs Free Energy. The molar excess Gibbs free energies of mixing (G^E) for DBE + cyclohexane and DBE + tetrachloromethane were calculated from the corresponding vapor pressure data at 298.15 K by using Barker's method (25). The second virial coefficients (β_{11} , β_{22}) of pure components were calculated from Berthelot's equation (27) using values of critical constants from literature (22). The values of β_{12} were assumed equal to $1/2(\beta_{11} + \beta_{22})$. The activity coefficients f_1 and f_2 and G^E values as a function of x_1 for the same set of mixtures are recorded in Table 2. The G^E values for both DBE + cyclohexane and DBE + tetrachloromethane are positive throughout the concentration range, and these values for cyclohexane are larger than those for tetrachloromethane mixtures (Figure 1). The G^E values at 298.15 K for the DBE + cyclohexane system are in good agreement at mole fractions $x_1 < 0.2$ and $x_1 > 0.8$, but in the intermediate range, our values are slightly greater (not exceeding 5%) than the values measured by Birdi et al. (8) at 293.15 K. This difference may be due the measurement of vapor pressure data at two different temperatures. For the DBE + tetrachloromethane system our experimental values are always lower than those measured by Birdi et al. (8). In the

Table 1. Isobaric Thermal Expansivities α , Molar Isobaric Heat Capacities C_p , Isothermal Compressibilities K_T , Densities ρ , Ultrasonic Speeds u , and Virial Coefficients β of Pure Components at 298.15 K (Observed Densities and Ultrasonic Speeds Given in Parentheses)

component	$\alpha \times 10^3/\text{K}^{-1}$	$C_p/(\text{J K}^{-1} \text{mol}^{-1})$	K_T/TPa^{-1}	$\rho \times 10^{-3}/(\text{kg m}^{-3})$	$u/(\text{m s}^{-1})$	$\beta \times 10^6/(\text{m}^3 \text{mol}^{-1})$
1,2-Dibromoethane (1)	0.9514 ^a	134.70 ^c	607 ^a	2.1702 (2.1701) ^e	990 (990) ^a	-1045.1 (-975.3) ^b
cyclohexane (2)	1.2170 ^b	155.45 ^b	1120 ^b	0.77390 (0.77392) ^b	1254 (1253) ^b	-1571.5 (-1466.1) ^b
tetrachloromethane (2)	1.2305 ^d	132.97 ^c	1067 ^c	1.58450 (1.58445) ^e	928 (927) ^d	-1418.5

^a Reference 23. ^b Reference 19. ^c Reference 22. ^d Reference 24. ^e Reference 18. ^f Reference 21. ^g Computed from molar volumes. ^h At 308.15 K.

Table 2. Pressure P , Activity Coefficients f_1 and f_2 of the Components, and Excess Molar Gibbs Free Energy G^E for DBE (1) + Cyclohexane (2) and DBE (1) + Tetrachloromethane (2) Mixtures

x_1	p/kPa	f_1	f_2	$G^E/(\text{J mol}^{-1})$	x_1	p/kPa	f_1	f_2	$G^E/(\text{J mol}^{-1})$
DBE (1) + Cyclohexane (2) at 298.15 K									
0.0000	13.019				0.5936	9.296	1.2610	1.5149	749
0.0897	12.276	2.7480	1.0101	248	0.6863	8.490	1.1570	1.7661	690
0.1674	11.761	2.3333	1.0348	422	0.7817	7.278	1.0779	2.1481	559
0.2887	11.007	1.8773	1.1033	624	0.8872	5.517	1.0218	2.8182	337
0.4044	10.380	1.5792	1.2093	739	0.9422	4.218	1.0060	3.3362	186
0.5127	9.854	1.3771	1.3582	777	1.0000	1.612			
$RTG_0 = 3102 \text{ J mol}^{-1}; RTG_1 = 218 \text{ J mol}^{-1}; RTG_2 = 163 \text{ J mol}^{-1}$									
DBE (1) + Tetrachloromethane (2) at 298.15 K									
0.0000	15.318				0.6056	9.326	1.2051	1.3369	564
0.0912	14.494	2.0732	1.0091	185	0.6820	8.403	1.1437	1.4699	531
0.1817	13.480	1.7896	1.0326	327	0.7728	7.183	1.0810	1.7108	452
0.2866	12.376	1.5733	1.0738	448	0.8758	5.490	1.0273	2.1793	298
0.3814	11.403	1.4350	1.1244	521	0.9426	4.017	1.0064	2.6851	155
0.4982	10.417	1.3041	1.2124	567	1.0000	1.612			
$RTG_0 = 2271 \text{ J mol}^{-1}; RTG_1 = 348 \text{ J mol}^{-1}; RTG_2 = 373 \text{ J mol}^{-1}$									

Table 3. Ultrasonic Speeds u , Isentropic Compressibilities K_s , and Excess Isentropic Compressibilities K_s^E for DBE (1) + Cyclohexane (2) and DBE (1) + Tetrachloromethane (2) at 298.15 K

x_1	$u/(\text{m s}^{-1})$	K_s/TPa^{-1}	K_s^E/TPa^{-1}	x_1	$u/(\text{m s}^{-1})$	K_s/TPa^{-1}	K_s^E/TPa^{-1}
DBE (1) + Cyclohexane (2)							
0.0000	1254	823	0.6002	1028	620	-10	
0.1071	1184	798	8	0.6960	1016	581	-13
0.1995	1136	774	11	0.7931	1004	545	-11
0.3034	1096	739	9	0.8852	996	511	-8
0.4003	1068	701	2	1.0000	990	470	
0.4906	1050	661	-7				
DBE (1) + Tetrachloromethane (2)							
0.0000	928	732	0.6302	978	539	-39	
0.1020	930	706	-17	0.7053	984	523	-34
0.2050	932	680	-29	0.8274	986	499	-23
0.3083	944	641	-38	0.8988	988	486	-14
0.4161	956	604	-42	1.0000	990	470	
0.5213	968	570	-43				

$$A = -20.24 \text{ TPa}^{-1}; B = -130.84 \text{ TPa}^{-1}; C = 38.97 \text{ TPa}^{-1}; D = 48.98 \text{ TPa}^{-1}; \sigma = 1.4 \text{ TPa}^{-1}$$

$$A = -171 \text{ TPa}^{-1}; B = 16 \text{ TPa}^{-1}; C = -2 \text{ TPa}^{-1}; \sigma = 1.68 \text{ TPa}^{-1}$$

intermediate range a nearly 20% difference is found; however, the agreement is better in the low and high mole fraction regions of DBE. The form of the function used for G^E , following Redlick and Kister (26), is

$$G^E = x_1 x_2 RT [G_0 + G_1(x_1 - x_2) + G_2(x_1 - x_2)^2] \quad (1)$$

where G_0 , G_1 , and G_2 are adjustable parameters. The values of these parameters along with G^E data for DBE + cyclohexane and DBE + tetrachloromethane mixtures at 298.15 K are given in Table 2.

Isentropic Compressibilities. The ultrasonic speeds for DBE + tetrachloromethane and DBE + cyclohexane mixtures for the whole mole fraction range at 298.15 K are reported in Table 3. The values of isentropic compressibility (K_s) were estimated from the experimentally observed ultrasonic speeds (u) and the densities (ρ) of the mixtures (evaluated from

already reported excess molar volume data) (29) by using the relation

$$K_s = (\rho u^2)^{-1} \quad (2)$$

Excess isentropic compressibility was calculated by using the equation

$$K_s^E = K_s - K_s^{\text{id}} \quad (3)$$

while K_s^{id} was obtained from the relation (28)

$$K_s^{\text{id}} = \sum_1 \phi_1 (K_{s,i} + TV_i \alpha_i^2 / C_{p,i}) - T \left(\sum_i (x_i V_i) \left(\sum_i \phi_i \alpha_i \right)^2 / \sum_i x_i C_{p,i} \right) \quad (4)$$

where ϕ_i is the volume fraction of component i in the mixture, referred to the unmixed state, x_i is the corresponding mole fraction, T is the temperature and $K_{s,i}$, V_i , α_i , and $C_{p,i}$ are, respectively, the isentropic compressibility, molar volume, isobaric thermal expansivity, and molar heat capacity for pure component i . The values of α_i and $C_{p,i}$ were taken from the literature (23, 19, 21, 22) (Table 1). The molar volumes were calculated from the densities of the pure components.

The K_s and K_s^E obtained from eqs 2 and 3 for these mixtures are reported in Table 3. These values of K_s^E were fitted to the equation

$$K_s^E/\text{TPa}^{-1} = x_1 x_2 [A + B(x_1 - x_2) + C(x_1 - x_2)^2 + D(x_1 - x_2)^3] \quad (5)$$

where A - D are adjustable parameters which fitted the equation. These parameters were calculated using the method of least squares and are reported in Table 3 along with standard deviations. No values of K_s^E for these mixtures are available, and hence comparison is not possible. Plots of K_s^E against mole fraction (x_1) for these mixtures are shown in Figure 2. K_s^E values for DBE + tetrachloromethane are negative throughout the mole fraction range; however, for DBE + cyclohexane, K_s^E values are positive up to 0.4 mole fraction of DBE and thereafter become negative.

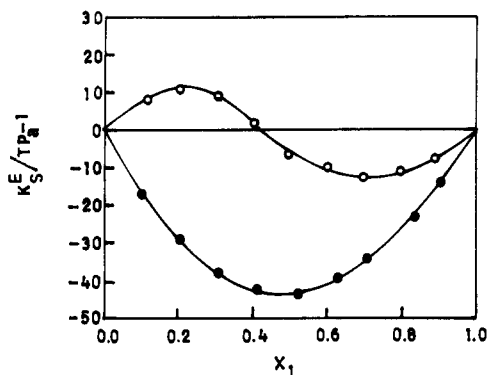


Figure 2. Excess isentropic compressibilities K_s^E at 298.15 K for (O) DBE (1) + cyclohexane (2) and (●) DBE (1) + tetrachloromethane (2).

The G^E , K_s , and K_s^E values were estimated using the Flory theory (15, 16), and reasonably good agreement was found between the experimental values and those calculated from the Flory theory. For instance, at 0.1, 0.5, and 0.9 mole fractions of DBE the experimental G^E values and the calculated G^E values (given in parentheses) for the DBE + cyclohexane system are 273 (462), 776 (1274), and 289 (508) J mol⁻¹, respectively, and for the DBE + tetrachloromethane system, they are 201 (166), 568 (442), and 251 (155) J mol⁻¹, respectively. Corresponding K_s values for the DBE + cyclohexane system are 802 (726), 658 (560), and 505 (453) TPa⁻¹, and for the DBE + tetrachloromethane system, they are 720 (758), 578 (597), and 485 (467) TPa⁻¹. The K_s^E values at these mole fractions are 8 (-34), -7 (-77), and -7 (-27) TPa⁻¹ for the DBE + cyclohexane system and -17 (-11), -43 (-18), and -14 (-6) TPa⁻¹ for the DBE + tetrachloromethane system.

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