Excess Thermodynamic Functions of the Systems Cyclohexane+Isomeric Xylenes

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The excess volumes V^E, excess heat capacities C_P^E and excess isothermal compressibilities β_T^E of cyclohexane+isomeric xylenes have been determined at 25, 40, and 50 °C. The results are discussed in the light of Flory's theory.

Studies on the excess thermodynamic functions of binary liquid mixtures throw considerable light in understanding the nature of molecular interactions. In these laboratories we have taken up a systematic study of the thermodynamic behaviour of a large number of binary mixtures containing reasonably simple molecules and test of the applicability of Flory's theory.[1,2] The present paper deals with the studies on the thermodynamic behaviour of the binary mixtures of *o*-xylene, *m*-xylene, and *p*-xylene with cyclohexane which form an interesting series of systems involving similar molecular structures which interact very weakly. The excess volumes V^E, excess heat capacities C_P^E, and the excess isothermal compressibilities β_T^E of the above binary systems have been studied and the results are analysed on the basis of Flory's theory.[3]

Experimental

Analytical reagent grade cyclohexane, *o*-xylene, *m*-xylene, and *p*-xylene were purified according to the standard procedures.[4] The densities of the purified samples determined at 25 °C using bicapillary type pycnometer with an accuracy of 2 in 10^5 are 0.77383, 0.87593, 0.85987, and 0.85673 g cm^{-3} respectively for cyclohexane, *o*-xylene, *m*-xylene, and *p*-xylene. These values are in good agreement with those reported in the literature.[5,6]

The excess volumes were measured directly using a mixing cell with an accuracy of ± 0.002 cm^3 mol^{-1}. The molar heat capacities at constant pressure were measured using an adiabatic calorimeter with an accuracy of $\pm 0.3\%$. Ultrasonic velocity in pure liquids and in binary mixtures was determined using a single crystal variable path interferometer working at 3MHz with an accuracy of $\pm 0.01\%$. The details of the above experimental techniques were discussed in our earlier communications.[1,2] The coefficient of thermal expansion (α) of pure liquids and their mixtures were determined from the experimentally determined density data at an interval of 5 °C in the range 20 to 60 °C.

Results

The experimental results of pure liquids are given in Table 1, along with literature values for comparison. The agreement between the two sets of values is quite good. The experimentally determined excess volume data (as many as a 15 sets of V^E values are obtained at each temperature covering the entire concentration range) of the binary mixtures of *o*-xylene,

Table 1. Pure liquid parameters

Temp / °C	u/ms^{-1}	$10^3\alpha$/K^{-1}	V / cm^3 mol^{-1}	C_P / J K^{-1} mol^{-1}	$\beta_T \times 10^6$ / bar^{-1}	v^* / cm^3 mol^{-1}	T^* / K	p^* / J cm^{-3}
			Cyclohexane					
25	1249.5	1.215	108.762	159.6	112.8	84.30	4723.9	534.88
	(1252.7)[c]			(156.5)[c]				
40	1177.5	1.264	110.796	163.6	129.0	84.47	4754.6	527.67
50	1129.2	1.294	112.185	166.0	141.1	84.66	4783.8	520.09
			o-Xylene					
25	1349.8	0.961	121.200	181.3	81.1	97.77	5348.4	543.12
	(1348.7)[b]	(0.963)[a]		(180.7)[d]				
40	1290.4	0.975	122.981	186.2	89.2	98.18	5423.3	536.95
50	1250.8	0.985	124.191	189.5	95.3	98.46	5472.6	531.30
			m-Xylene					
25	1321.1	1.009	123.470	178.3	87.7	98.81	5204.4	536.03
	(1323.1)[b]	(1.004)[a]		(176.2)[d]				
40	1258.3	1.025	125.403	182.7	97.2	99.26	5278.7	527.10
50	1216.7	1.036	126.693	185.6	104.3	99.58	5329.7	519.64
			p-Xylene					
25	1309.7	1.015	123.930	181.3	89.1	99.08	5188.5	531.59
	(1309.8)[b]	(1.017)[a]		(181.3)[d]				
40	1248.3	1.037	125.851	185.9	98.9	99.43	5247.1	526.18
50	1207.4	1.045	127.167	189.0	105.9	99.80	5305.4	517.74

a) Ref. 6. b) Extropolated value of Ref. 11. c) Ref. 12. d) Ref. 13.

Table 2. Parameters of Eq. 1 and standard deviation of excess volumes

Temp °C	a_0	a_1	a_2	σ / cm mol^{-1}
		Cyclohexane+*o*-Xylene		
25	2.0555	−0.5161	−0.0359	0.003
40	2.1928	−0.8033	0.2606	0.004
50	2.2831	−0.8085	0.4509	0.003
		Cyclohexane+*m*-Xylene		
25	2.5566	−0.5251	0.4050	0.003
40	2.7426	−0.5216	0.0951	0.002
50	2.8206	−0.5563	0.1571	0.003
		Cyclohexane+*p*-Xylene		
25	2.2809	−0.6584	0.5129	0.002
40	2.3667	−0.7375	0.4499	0.004
50	2.4536	−0.7146	0.4356	0.001

m-xylene, and *p*-xylene with cyclohexane were fitted to the equation of the form

$$V^E/x_1x_2 = [a_0+a_1(x_2-x_1)+a_2(x_2-x_1)^2], \quad (1)$$

where x_1 and x_2 are the mole fractions of cyclohexane and xylenes respectively. Values of the coefficients determined using the method of least squares are listed in Table 2. The last column of the table contains values of σ, the standard deviation of the fit in each case. The excess volumes of these systems were studied previously by Reddy *et al.*[8] and Jain *et al.*[7] The accuracy of the experimental excess volumes reported by Reddy *et al.*[8] is ± 0.05 cm^3 mol^{-1}. Further they have studied the *p*-xylene system at 32.5 °C, *m*-xylene system at 34 °C, and *o*-xylene system at 35 °C. In view of this, a direct comparison with the values of the present investigation has not been attempted. The excess volumes of Jain *et al.*[7] are slightly higher than the present ones. However no importance has been given to this discrepancy since Jain *et al.*[7] have not stated the errors involved in their measurements. The results of measurement of u, C_p, α, and β_T of binary mixtures of cyclohexane with isomeric xylenes are presented in Table 3.

Discussion

The experimental excess functions are examined in this section for the binary mixtures in the light of Flory's theory. The excess functions V^E, H^E, and β_T^E are related to the properties of pure components *via* the relations

$$H^E = x_1v_1{}^*p_1{}^*\left(\frac{1}{\tilde{v}_1}-\frac{1}{\tilde{v}}\right) + x_2v_2{}^*p_2{}^*\left(\frac{1}{\tilde{v}_2}-\frac{1}{\tilde{v}}\right) + x_1v_1{}^*\theta_2X_{12}/\tilde{v} \quad (2)$$

$$\beta_T^E = \frac{3\tilde{v}^2(\tilde{v}^{1/3}-1)}{p^*[1-3(\tilde{v}^{1/3}-1)]} - \frac{1}{\tilde{v}}[\phi_1\tilde{v}_1\beta_{T_1}+\phi_2\tilde{v}_2\beta_{T_2}] \quad (3)$$

$$p^* = \phi_1p_1{}^* + \phi_2p_2{}^* - \phi_1\theta_2X_{12} = \frac{T\tilde{v}^{4/3}}{(\tilde{v}^{1/3}-1)}\left[\frac{\phi_1p_1{}^*}{T_1{}^*}+\frac{\phi_2p_2{}^*}{T_2{}^*}\right], \quad (4)$$

where

$$\tilde{v} = \phi_1\tilde{v}_1 + \phi_2\tilde{v}_2 + V^E/(x_1v_1{}^*+x_2v_2{}^*), \quad (5)$$

where v_1 and v_2 are the reduced volumes, $v_1{}^*$ and $v_2{}^*$ are the characteristic volumes, $p_1{}^*$ and $p_2{}^*$ are the characteristic pressures, and β_{T1} and β_{T2} are the isothermal compressibilities of the pure components. $\tilde{v}$, p^*, and θ_2 X_{12} are the reduced volume, characteristic pressure and the interaction energy parameter respectively of the mixture.

The interaction energy parameter of the mixture X_{12} which is a measure of the difference of interaction energy between the unlike pairs and the mean of like pairs, can be evaluated using any experimental excess function. This value of X_{12} can be used to evaluate theoretically the other excess functions. The interaction energy term involves implicitly in the expression for V^E and explicitly in that for H^E. Hence it may appear logical to evaluate X_{12} using H^E rather than V^E data. However in view of the higher accuracy of the experimental V^E data and its availability over comparatively wide temperature and concentration range X_{12} has been evaluated *via* V^E in the present work.

According to Flory's theory at any given temperature X_{12} should be a constant independent of the composition of the mixture. An examination of the data presented in Table 4 indicates that X_{12} is reasonably constant at

Table 3. Properties of binary solutions

x_2	u/ms^{-1}			$10^3\alpha$/K^{-1}			C_p/J mol^{-1}			$10^6\beta_T$/bar^{-1}		
	25 °C	40 °C	50 °C	25 °C	40 °C	50 °C	25 °C	40 °C	50 °C	25 °C	40 °C	50 °C
					Cyclohexane+*o*-Xylene							
0.2502	1265.5	1197.3	1151.8	1.163	1.098	1.038	164.1	168.2	171.5	105.9	118.8	129.5
0.4978	1284.8	1219.1	1175.2	1.185	1.117	1.054	169.3	174.1	177.2	98.8	109.3	118.0
0.7497	1296.4	1240.5	1194.6	1.198	1.129	1.066	175.3	180.0	183.3	91.5	100.7	106.9
					Cyclohexane+*m*-Xylene							
0.2480	1258.9	1189.2	1142.7	1.167	1.128	1.064	163.0	167.5	170.1	107.7	121.2	132.0
0.4989	1274.4	1207.5	1162.7	1.190	1.148	1.082	167.2	172.1	174.9	102.0	114.1	123.4
0.7505	1295.4	1231.0	1187.2	1.213	1.162	1.103	172.8	177.2	180.3	94.7	105.4	116.1
					Cyclohexane+*p*-Xylene							
0.2585	1256.2	1188.6	1143.8	1.168	1.117	1.064	164.2	168.3	171.5	107.9	121.1	131.1
0.4973	1268.7	1201.5	1156.4	1.188	1.140	1.082	169.2	175.9	176.8	102.1	114.4	123.7
0.7463	1273.5	1212.4	1165.4	1.203	1.154	1.099	175.1	179.6	182.9	97.1	107.8	117.1

TABLE 4. COMPARISON OF β_T^E WITH FLORY'S THEORY

T °C	x_2	X_{12} J cm^{-3}	X_{12} mean	$\beta_T^E \times 10^6$/bar^{-1} Exptl	Calcd	C_P^E J K^{-1} mol^{-1}
		Cyclohexane+*o*-Xylene				
25	0.2502	36.59		5.3	3.9	1.1
	0.4978	36.28	35.57	5.4	4.2	1.1
	0.7497	33.85		2.4	2.3	1.4
40	0.2502	38.54		5.8	4.7	1.0
	0.4978	36.30	36.65	5.8	4.6	0.7
	0.7497	35.11		2.6	2.5	0.5
50	0.2502	39.62		6.3	4.2	0.3
	0.4978	36.88	37.69	6.2	4.9	0.5
	0.7497	36.57		1.3	2.7	0.3
		Cyclohexane+*m*-Xylene				
25	0.2480	41.03		1.5	4.5	−1.2
	0.4989	38.78	40.19	3.1	5.9	−1.7
	0.7505	40.75		1.6	3.8	−0.8
40	0.2480	38.09		1.0	4.7	−0.8
	0.4989	38.22	38.13	3.7	7.7	−1.0
	0.7505	38.07		1.3	4.0	−0.7
50	0.2480	38.82		1.7	6.7	−0.7
	0.4989	38.31	38.45	2.5	7.3	−0.8
	0.7505	38.23		2.0	3.6	−0.4
		Cyclohexane+*p*-Xylene				
25	0.2585	36.77		2.0	3.3	−1.0
	0.4973	34.53	35.19	2.3	3.4	−1.2
	0.7463	34.28		2.8	3.4	−0.8
40	0.2585	36.58		3.2	5.8	−1.0
	0.4973	33.04	34.02	1.6	5.8	−0.6
	0.7463	32.45		2.3	3.5	−0.6
50	0.2585	35.62		0.5	6.0	−0.4
	0.4973	33.01	34.13	1.9	6.2	−0.7
	0.7463	33.75		3.4	3.9	−0.3

any particular temperature. Hence the mean value of X_{12} is used to evaluate the excess functions at any given temperature.

The theoretically evaluated excess isothermal compressibilities β_T^E using Eq. 3 are compared with the experimental β_T^E in Table 4. The agreement between the two sets of data is not satisfactory. This disagreement may be attributed to the slight polarity of xylenes. Similar disagreement was also noticed between theoretical and experimental excess parameters of benzene+isomeric xylenes[9] and toluene+isomeric xylenes.[10]

In view of non availability of experimental H^E data for the systems under study at all temperatures and concentrations an attempt is made however to compare the data at 25 °C for equimolar concentrations as can be seen from Table 5. The agreement is not quite good reflecting the inadequacy of Flory's theory in predicting excess functions for these systems under study.

TABLE 5. COMPARISON OF EXPERIMENTAL AND THEORETICAL EXCESS HEATS FOR EQUIMOLAR SOLUTIONS AT 25 °C

System	H^E Calcd	Exptl
Cyclohexane+*o*-Xylene	814	523[a]
Cyclohexane+*m*-Xylene	912	576[b]
Cyclohexane+*p*-Xylene	809	487[a]

a) Evaluated from X_{12} values of Ref. 7. b) Data of Ref. 14.

TABLE 6. COMPARISON OF EXPERIMENTAL AND THEORETICAL EXCESS HEAT CAPACITIES FOR EQUIMOLAR MIXTURES ($x_2 \simeq 0.5$) AT 37.5 °C

System	C_P^E/J K^{-1} mol^{-1} Exptl	Calcd
Cyclohexane+*o*-Xylene	0.7±0.5	1.7±0.8
Cyclohexane+*m*-Xylene	−1.0±0.5	−1.7±0.8
Cyclohexane+*p*-Xylene	−1.3±0.8	−0.9±0.5

Flory's theory is also useful in predicting the excess heat capacities. The excess heat capacities are related to excess enthalpies *via* the relation

$$C_P^E = \left(\frac{\partial H^E}{\partial T}\right)_p \qquad (6)$$

using Eq. 2 excess enthalpies have been evaluated at 25, 40, and 50 °C. $(\partial H^E/\partial T)_P$ has been evaluated using H^E data at 25 and 50 °C which gives the value of C_P^E at 37.5 °C. The value of C_P^E so evaluated at 37.5 °C for the equimolar solutions are compared in Table 6, with C_P^E values obtained by intrapolating the experimental C_P^E data which are given in Table 4. The agreement between experimental and theoretical C_P^E values is quite good.

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