Enthalpy of Mixing of Methanol + Benzene + Mercuric Chloride at 303.15 K

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Enthalpy of mixing of the binary system involving methanol + benzene was investigated at 303 ± 0.1 K. The excess enthalpy for various mole fractions of methanol remained positive, illustrating the expenditure of extra energy for breaking the intermolecular association of methanol in order to homogenize it with the nonpolar benzene. The influence of mercuric chloride, dissolved in methanol, on the excess enthalpy of this system was examined by varying the salt concentration. A significant increase in the excess enthalpy was observed with an increase in the salt concentration compared to that of the salt-free system, establishing additional expenditure of energy. It was proved unambiguously that a coordination sphere of Hg^{2+} ions is present and that these are expelled during the homogenization of methanol with benzene.

Introduction

In recent years there has been considerable progress in the experimental investigation of the excess thermodynamic properties of liquid mixtures. Excess thermodynamic functions have been used as a qualitative guide to predict the extent of complex formation in binary liquid mixtures. In phase equilibria the addition of salt in a liquid mixture is believed to be due to the formation of associated complexes (Long and McDevit, 1952). Upon addition of salts to liquid mixtures significant change in the free energy of the liquid is expected. Since there is an interrelation between the excess free energy and the excess enthalpy of liquid mixtures, addition of salts can be expected to bring about a change in the excess enthalpy values of liquid mixtures. Very few works on the effect of salts on the enthalpy of mixing have been reported in the literature (Rajendran et al., 1988, 1989a,b, 1991; Rajendran and Srinivasan, 1994; Nowicka and Taniewska-Osinska, 1997). As a part of an ongoing program in this area (Dharmendira Kumar and Rajendran, 1998) we have recently conducted an experimental investigation on the effect of mercuric chloride on the excess enthalpy of mixing of the binary system methanol + benzene. The chloride salt was chosen in view of its significant effect on the vapor−liquid equilibrium relationship of this system.

The experimentation was carried out at (303.15 ± 0.1) K, and at this temperature the material losses due to vaporization were taken to be insignificant.

Experimental Section

Chemicals Used. All components used in this work are analytical reagent grade supplied by E. Merck. The solvent was further purified by fractional distillation (Furniss et al., 1989), and the salt was kept in a desiccator for more than 24 h before use. The purities of the compounds were checked by comparing measured densities and boiling points with those reported in the literature (Riddick et.al, 1986; Timmermans, 1980). Densities were measured using a bicappillary pycnometer, and boiling points were measured using an ebulliometer giving an accuracy of ±0.2 K. The measured values are given in Table 1, along with the literature values.

Table 1. Physical Properties of the Solvents Used

	boiling point, T_b/K		ρ/(g cm^{-3})	
solvents	this work	lit. (Timmermans, 1980)	this work	lit. (Timmermans, 1980)
methanol	337.72	337.70	0.7890	0.7900
benzene	353.14	353.10	0.8761	0.8765

Apparatus Used. The calorimeter used in this work is basically of the type employed by earlier workers (Tsao and Smith, 1953; Murti and Van Winkle, 1957). The description of the apparatus is given in one of our earlier papers (Rajendran et al., 1989). The performance of the calorimeter and its reliability for the measurement of the enthalpy of mixing were ascertained by determining the enthalpy of mixing values of benzene + cyclohexane at 303.15 K. The data obtained in the present work compared well within 2% with the literature data (Mrazek and Van Ness, 1961; Figure 1).

Preparation of Salt Solutions. The mercuric chloride was first dissolved to the desired level of concentration in methanol, in which it is preferentially soluble at the experimental temperature. The concentrations reported in this work, i.e., 5%, 10%, are the initial concentrations by mass [mass of salt/(mass of salt + mass of methanol)] in the methanol component. Some of the experimental runs were repeated to check the reproducibility of the data, and they were found to be within ±3%. The maximum salt concentration prepared was 10 mass %. In this system, the salt mercuric chloride is highly soluble in methanol and sparingly soluble in benzene (478 g of $HgCl_2$/(L of methanol) and 2.0 g of $HgCl_2$/(L of benzene)).

Procedure. The experimental procedure adopted in this work is similar to the one reported by (Tsao and Smith, 1953). The procedure is described in our earlier paper (Rajendran et al., 1989). However, some details of the experimental procedure utilized are summarized below. The values of the enthalpies of mixing were registered by

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Table 2. Excess Enthalpy of the System Methanol (1) + Benzene (2) + Mercuric Chloride (3)[a]

x_1	H^E/(J·mol^{-1})	δH^E/(J·mol^{-1})	x_1	x_3	H^E/(J·mol^{-1})	x_1	x_3	H^E/(J·mol^{-1})
0.104	584.37	589.40	0.101	8.96×10^{-5}	669.44	0.182	1.69×10^{-4}	958.59
0.182	797.72	783.95	0.184	3.50×10^{-4}	848.93	0.301	6.39×10^{-4}	1050.05
0.313	884.91	881.44	0.309	8.87×10^{-4}	945.16	0.397	1.65×10^{-3}	1078.63
0.410	889.10	893.24	0.397	1.34×10^{-3}	949.43	0.462	2.49×10^{-3}	1057.54
0.473	880.39	885.50	0.464	2.22×10^{-3}	928.38	0.515	4.02×10^{-3}	1012.52
0.527	849.35	867.21	0.521	2.92×10^{-3}	888.84	0.561	9.56×10^{-3}	984.78
0.574	821.31	842.19	0.566	6.24×10^{-3}	856.04	0.603	1.38×10^{-2}	941.52
0.613	803.41	813.24	0.605	8.76×10^{-3}	828.34	0.631	1.81×10^{-2}	895.58
0.667	753.20	750.14	0.630	1.15×10^{-2}	810.18	0.653	2.37×10^{-2}	862.19
0.691	733.87	717.17	0.681	1.56×10^{-2}	764.41	0.704	3.59×10^{-2}	789.56
0.795	541.57	540.11	0.812	2.29×10^{-2}	527.60	0.759	4.72×10^{-4}	711.32
0.810	464.38	475.63	0.847	3.10×10^{-2}	450.78	0.832	6.17×10^{-2}	527.60
0.879	300.95	413.42	0.871	3.31×10^{-2}	371.12	0.877	6.98×10^{-2}	418.44
0.920	209.57	219.11	0.954	4.46×10^{-2}	162.42	0.902	8.06×10^{-2}	335.22

[a] x_1, mole fraction; x_3, mass fraction.

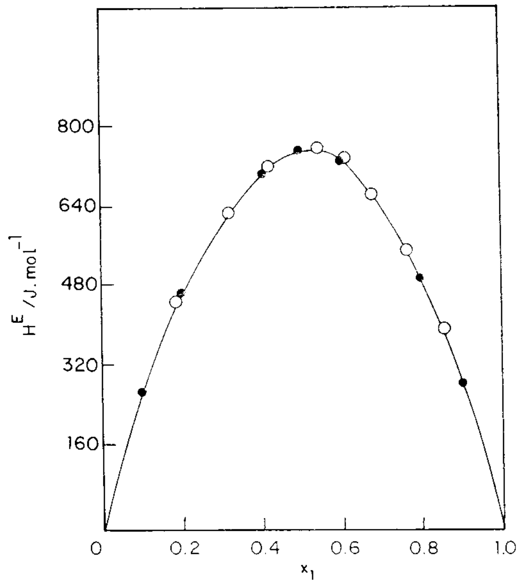

Figure 1. Enthalpy of mixing for the system benzene + cyclohexane at 303.15 K: this work (○); Mrazek and Van Ness (1961; ●).

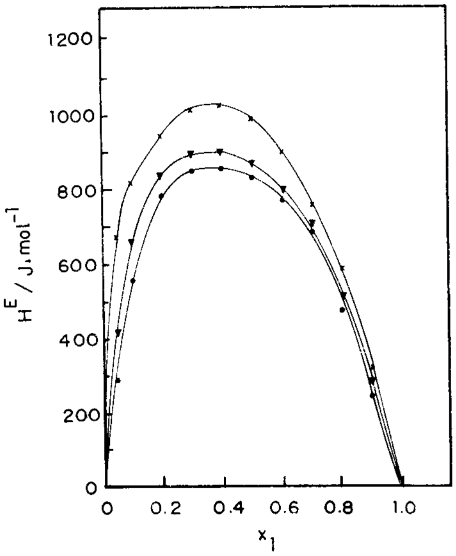

Figure 2. Effect of mercuric chloride on the enthalpy of mixing of methanol + benzene: salt-free (●); 5 mass % mercuric chloride (▼); 10 mass % mercuric chloride (×).

the microprocessor based unit (MIPROC), which has a built-in program to supply and measure the equivalent electrical energy fed to the liquid mixture and to determine the values of enthalpy of mixing and display them digitally in joules. The value displayed by the MIPROC is divided by the total number of moles of the liquid mixture taken in the calorimeter to obtain the enthalpy of mixing values in joules per mole. The total volume of the calorimeter is 215 cm^3.

Results and Discussion

As shown in Figure 2, the enthalpy of mixing for the methanol + benzene (salt-free) system increases with an increase in the mole fraction of methanol from 0.104 to 0.613. But further increase in the mole fraction decreases the enthalpy value. This may be attributed to the fact that methanol is polar and benzene nonpolar and hence the miscibility requires the polarization of benzene by the methanol dipole to aid dipole-induced dipole interaction dependent association. At the lower concentration of methanol the increase in the values of excess enthalpy shows the expenditure of energy for breaking the inherent intermolecular hydrogen bonding in methanol and orienting methanol dipoles for benzene polarization. With an increase in the mole fraction of methanol such energy expenditure registers more and more as an increase in the excess enthalpy values. This can be observed up to 0.613 mole fraction of methanol. Further increase in the methanol concentration registered a decrease in the value of excess enthalpy. This may be due to the fact that the availability of benzene molecules becomes lesser and lesser for any extra expenditure of energy toward association with methanol.

When the salt mercuric chloride is added to methanol, the excess enthalpy of the methanol + benzene + mercuric chloride system shows a further increase in the value of excess enthalpy, as shown in Figure 2. This may be due to the following reason. In the solution of mercuric chloride in methanol there are free methanol and coordinated methanol. During mixing, only free methanol will enter an association process with benzene, producing a positive enthalpy of mixing. As a result of the decrease in free methanol content during mixing, some of the weakly bonded methanol will escape from the coordination sphere of the ions and this process would favor formation of mercuric chloride clusters (Long and McDevit, 1952). Since every additional salt solution of methanol introduces extra free methanol, the enthalpy of mixing becomes more and more positive up to 0.464 mole fraction of methanol. An interesting observation here is that for every mole fraction of methanol the enthalpy of mixing in the salt-free methanol + benzene system is less than that of the mercuric chloride containing system, supporting the energy expen-

Table 3. Scatchard Model Constants for the Salt-Free System Methanol (1) + Benzene (2)

A_0	837.706	A_3	−594.033
A_1	−164.354	A_4	169.1152
A_2	347.843		

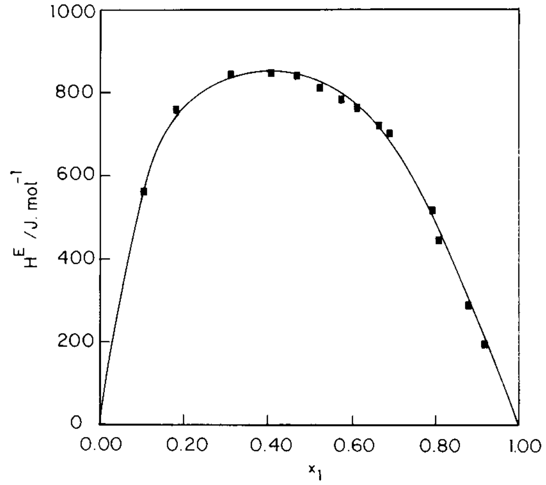

Figure 3. Correlation of data on enthalpy of mixing for the system methanol + benzene (salt-free): experimental result (■); Scatchard model (—).

diture toward removal of methanol from the coordination sphere of either Hg^{2+} or Cl^-. The decrease in excess enthalpy beyond 0.464 methanol mole fraction equal to 0.464 is being attributed to a lower and lower benzene content for methanol association (Table 2).

Correlation of the Experimental Data. Scatchard Model. The experimental enthalpy of mixing data for the system methanol + benzene have been correlated by the Scatchard model (Scatchard et al., 1952).

$$H^E = x_1x_2[A_0 + A_1(x_1 - x_2) + A_2(x_1 - x_2)^2 + ...] \quad (1)$$

where x_1 and x_2 are the mole fractions of components 1 and 2, respectively, and the A's are the constants that are functions of temperature and the system properties. The values of the constants obtained are given in Table 3.

The values of excess enthalpy data calculated on the basis of the Scatchard model are shown in Figure 3. It may be observed that the Scatchard model fits the experimental data well.

Conclusion

The enthalpies of mixing of the methanol + benzene system for both salt-free and mercuric chloride salt systems were investigated. For both situations positive values of the enthalpy of mixing were observed. In the salt-free system the ability of polar methanol to associate with nonpolar benzene via polarization would require prior inhibition of the intermolecular association of methanol by an expenditure of energy. The positive value of the enthalpy of mixing supported this conclusion.

The same positive but higher value of the enthalpy of mixing observed when the salt is added evidently confirms the existence of methanol−Hg^{2+} complexes prior to the mixing of methanol with benzene. This may be due to the requirement of an additional expenditure of energy that could be required to liberate the coordinated methanol from the coordination sphere of Hg^{2+} in order to bring it into association with benzene.

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