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# STUDIES ON THE THERMODYNAMIC PROPERTIES OF BINARY MIXTURES CONTAINING AN ALCOHOL. XIII. EXCESS MOLAR ENTHALPIES OF SOME MIXTURES OF *n*-ALCOHOLS WITH ANILINE OR CHLOROBENZENE AT 298.15 K *

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## ABSTRACT

The excess molar enthalpies, $H^E$, were obtained as a function of the mole fraction, $x$, at 298.15 K and atmospheric pressure for each of the mixtures of methanol, ethanol, *n*-propanol or *n*-pentanol with aniline or chlorobenzene, and also for *n*-hexanol + chlorobenzene. The values of $H^E$ are positive in all the mixtures except those of methanol or ethanol + aniline, in which the excess molar enthalpies show sigmoid-shaped curves. The results were discussed in terms of the effects due to the dissociation, association and chain length of the alcohols and different substituents in the benzene ring.

## INTRODUCTION

In recent years there has been a keen interest in the concept of the functional group effect in the formation of multiple hydrogen-bonded complexes. An early suggestion for this effect was to explain the structure of liquid water. It was consequently believed that the lower alcohols should also possess a degree of the effect in the formation of hydrogen-bonded complexes. Further, it was realized that thermodynamic data could clearly show the functional group effect in solutions.

As a continuation of our studies on the thermodynamic properties of binary mixtures containing an alcohol [1–5], we report here the excess molar enthalpies of four *n*-alcohols with aniline and five *n*-alcohols with chlorobenzene at 298.15 K. The interactions between like and unlike molecules are discussed, and possible geometries of the complexes in the mixtures described.

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## EXPERIMENTAL

### Apparatus

A Picker flow microcalorimeter was used to measure the excess molar enthalpies. Details of the equipment and of the operating procedure have been described in our earlier work [6]. The technique and calibration were first checked by measuring the known value of $H^{\mathrm{E}}$ for the mixture benzene + cyclohexane at 298.15 K. Our results were within 1% of the values reported by Grolier [7] at $x = 0.5$.

### Materials

The chemicals used were the same as those used in our previous studies [4]. All samples were treated prior to use by the methods of Riddick and Bunger [8]. The refractive indexes $n_{\mathrm{d}}^{25}$ and densities of pure liquids were in agreement with the literature values [8].

## RESULTS

The excess molar enthalpies at 298.15 K and atmospheric pressure for all mixtures are listed in Tables 1 and 2. The results were fitted by the least squares method to the equation

$$H^{\mathrm{E}} = x(1-x)\sum_{i=0}^{n} A_i(1-2x)^i \tag{1}$$

for alcohols with aniline and to the equation

$$H^{\mathrm{E}} = x(1-x)\sum_{i=0}^{n} A_i x^{i/2} \tag{2}$$

for alcohols with chlorobenzene so as to represent skewed results. The coefficients $A_i$ for eqns. (1) and (2) are listed in Table 3, and standard deviations are also given in the last column. Plots of excess molar enthalpies against mole fractions for these two series are shown in Figs. 1 and 2, and the variations of $H^{\mathrm{E}}$ with size of the alcohol molecule at $x = 0.5$ are shown in Fig. 3. The experimental results of *n*-butanol with chlorobenzene or aniline [4] are included in the figures for comparison.

As far as we know, only the excess molar enthalpies for methanol + aniline and ethanol, *n*-propanol + chlorobenzene have been measured previously [9–11]. The $H^{\mathrm{E}}$ values for methanol + aniline from the present study are in fair agreement with those reported by Deshpande and Pandya [9], but the

TABLE 1

Excess enthalpies, $H^E$, for binary mixtures of $n$-alcohols + aniline at 298.15 K
$x$ is the mole fraction of the $n$-alcohol.

| $x$ | $H^E$ (J mol$^{-1}$) | $x$ | $H^E$ (J mol$^{-1}$) | $x$ | $H^E$ (J mol$^{-1}$) |
|---|---|---|---|---|---|
| $x CH_3OH + (1-x) C_6H_5NH_2$ | | | | | |
| 0.0471 | 10.1 | 0.4345 | −135.4 | 0.8061 | −244.4 |
| 0.0846 | 14.2 | 0.5008 | −174.4 | 0.8417 | −232.9 |
| 0.1205 | 14.5 | 0.5609 | −203.2 | 0.8748 | −214.2 |
| 0.1549 | 9.61 | 0.6157 | −225.2 | 0.9057 | −187.3 |
| 0.1879 | 1.21 | 0.6658 | −241.2 | 0.9345 | −148.2 |
| 0.2500 | −23.4 | 0.7119 | −245.2 | 0.9616 | −99.3 |
| 0.3077 | −57.3 | 0.7544 | −251.3 | 0.9788 | −60.8 |
| 0.3611 | −92.4 | 0.7809 | −249.5 | | |
| $x C_2H_5OH + (1-x) C_6H_5NH_2$ | | | | | |
| 0.0425 | 91.6 | 0.4244 | 387.9 | 0.7697 | 153.9 |
| 0.0938 | 180.6 | 0.4809 | 360.2 | 0.8108 | 118.2 |
| 0.1432 | 248.9 | 0.5347 | 328.2 | 0.8503 | 79.3 |
| 0.1908 | 303.5 | 0.5860 | 294.2 | 0.8882 | 43.1 |
| 0.2590 | 362.3 | 0.6351 | 260.3 | 0.9246 | 14.1 |
| 0.3237 | 389.3 | 0.6819 | 221.6 | 0.9597 | −4.4 |
| 0.3851 | 397.8 | 0.7267 | 189.2 | 0.9823 | −8.0 |
| $x C_3H_7OH + (1-x) C_6H_5NH_2$ | | | | | |
| 0.0374 | 145.5 | 0.4205 | 778.3 | 0.7217 | 565.2 |
| 0.0783 | 278.2 | 0.4734 | 779.3 | 0.7684 | 487.8 |
| 0.1385 | 442.4 | 0.5251 | 767.8 | 0.8142 | 406.5 |
| 0.1974 | 569.9 | 0.5758 | 740.4 | 0.8592 | 316.9 |
| 0.2550 | 657.6 | 0.6254 | 693.2 | 0.9032 | 222.9 |
| 0.3114 | 722.3 | 0.6740 | 636.7 | 0.9464 | 125.5 |
| 0.3665 | 761.3 | | | | |
| $x C_5H_{11}OH + (1-x) C_6H_5NH_2$ | | | | | |
| 0.0325 | 206.1 | 0.3468 | 993.4 | 0.7175 | 765.3 |
| 0.0624 | 359.3 | 0.3970 | 1020.2 | 0.7743 | 642.3 |
| 0.1079 | 550.3 | 0.4481 | 1022.7 | 0.8322 | 495.2 |
| 0.1541 | 700.2 | 0.5001 | 1009.0 | 0.8911 | 325.2 |
| 0.2011 | 804.5 | 0.5530 | 981.3 | 0.9310 | 209.1 |
| 0.2488 | 886.7 | 0.6069 | 938.4 | 0.9714 | 85.4 |
| 0.2974 | 948.4 | 0.6617 | 855.6 | | |

signs of $H^E$ in the two papers are completely opposite. As to ethanol, $n$-propanol + chlorobenzene, our experimental values correspond with those of Nicolaides and Eckert [10] and Nagata and Tamura [11].

TABLE 2

Excess enthalpies, $H^E$, for binary mixtures of *n*-alcohols + chlorobenzene at 298.15 K; $x$ is the mole fraction of the *n*-alcohol.

| $x$ | $H^E$ (J mol$^{-1}$) | $x$ | $H^E$ (J mol$^{-1}$) | $x$ | $H^E$ (J mol$^{-1}$) |
|---|---|---|---|---|---|
| $x\mathrm{CH_3OH}+(1-x)\mathrm{C_6H_5Cl}$ | | | | | |
| 0.0324 | 184.1 | 0.4009 | 538.4 | 0.7467 | 243.9 |
| 0.0711 | 338.3 | 0.4468 | 513.2 | 0.7831 | 208.5 |
| 0.1079 | 440.1 | 0.4894 | 483.8 | 0.8164 | 166.8 |
| 0.1432 | 505.1 | 0.5292 | 453.3 | 0.8475 | 132.8 |
| 0.1769 | 540.8 | 0.5663 | 424.5 | 0.8763 | 103.3 |
| 0.2092 | 560.2 | 0.6178 | 377.5 | 0.9032 | 78.9 |
| 0.2401 | 573.4 | 0.6646 | 332.6 | 0.9283 | 56.2 |
| 0.2981 | 573.8 | 0.7074 | 287.7 | 0.9519 | 37.1 |
| 0.3515 | 565.2 | | | | |
| $x\mathrm{C_2H_5OH}+(1-x)\mathrm{C_6H_5Cl}$ | | | | | |
| 0.0511 | 419.9 | 0.3209 | 729.2 | 0.6775 | 374.5 |
| 0.0786 | 531.3 | 0.3633 | 710.9 | 0.7205 | 309.7 |
| 0.1054 | 602.7 | 0.4039 | 686.6 | 0.7613 | 249.3 |
| 0.1316 | 649.9 | 0.4429 | 657.3 | 0.8001 | 194.9 |
| 0.1571 | 689.6 | 0.4804 | 627.1 | 0.8371 | 142.2 |
| 0.1821 | 710.5 | 0.5339 | 569.3 | 0.8722 | 96.5 |
| 0.2305 | 733.3 | 0.5805 | 508.5 | 0.9058 | 59.3 |
| 0.2767 | 738.1 | 0.6323 | 439.9 | 0.9381 | 30.1 |
| $x\mathrm{C_3H_7OH}+(1-x)\mathrm{C_6H_5Cl}$ | | | | | |
| 0.0408 | 474.1 | 0.3109 | 884.1 | 0.6735 | 527.6 |
| 0.0631 | 583.1 | 0.3491 | 883.3 | 0.7192 | 450.1 |
| 0.0852 | 655.1 | 0.3864 | 867.8 | 0.7636 | 371.8 |
| 0.1068 | 711.5 | 0.4229 | 849.3 | 0.8067 | 301.2 |
| 0.1283 | 751.4 | 0.4762 | 806.7 | 0.8486 | 231.1 |
| 0.1495 | 782.2 | 0.5278 | 748.2 | 0.8892 | 163.9 |
| 0.1913 | 825.9 | 0.5779 | 687.1 | 0.9289 | 104.9 |
| 0.2321 | 855.4 | 0.6264 | 604.5 | 0.9547 | 65.1 |
| $x\mathrm{C_5H_{11}OH}+(1-x)\mathrm{C_6H_5Cl}$ | | | | | |
| 0.0296 | 370.6 | 0.2640 | 961.2 | 0.5758 | 807.9 |
| 0.0461 | 490.2 | 0.2980 | 972.7 | 0.6290 | 726.6 |
| 0.0627 | 580.7 | 0.3322 | 981.1 | 0.6825 | 633.9 |
| 0.0959 | 713.3 | 0.3666 | 980.4 | 0.7364 | 537.9 |
| 0.1292 | 800.2 | 0.4011 | 969.5 | 0.7906 | 432.3 |
| 0.1627 | 863.7 | 0.4357 | 950.9 | 0.8452 | 320.9 |
| 0.1963 | 906.2 | 0.4705 | 928.3 | 0.9001 | 204.7 |
| 0.2301 | 939.5 | 0.5230 | 873.4 | 0.9555 | 91.8 |

TABLE 2 (continued)

| $x$ | $H^E$ (J mol$^{-1}$) | $x$ | $H^E$ (J mol$^{-1}$) | $x$ | $H^E$ (J mol$^{-1}$) |
|---|---|---|---|---|---|
| $x C_6H_{13}OH + (1-x)C_6H_5Cl$ | | | | | |
| 0.0262 | 368.5 | 0.2407 | 928.3 | 0.5492 | 832.8 |
| 0.0408 | 479.6 | 0.2701 | 946.7 | 0.6046 | 753.1 |
| 0.0556 | 563.5 | 0.3059 | 967.6 | 0.6619 | 656.3 |
| 0.0854 | 678.2 | 0.3391 | 972.1 | 0.7192 | 550.9 |
| 0.1156 | 755.8 | 0.3729 | 967.2 | 0.7822 | 432.3 |
| 0.1482 | 817.7 | 0.4071 | 959.8 | 0.8395 | 322.1 |
| 0.1773 | 862.2 | 0.4419 | 940.5 | 0.9017 | 199.1 |
| 0.2088 | 900.1 | 0.4949 | 896.8 | 0.9440 | 113.9 |

## DISCUSSION

Although aniline and chlorobenzene resemble each other in structure, the experimental results obtained for the two series are very different in magnitude and shape. For alcohols + chlorobenzene, the $H^E$ values are all positive over the entire composition range and the mixing curves are skewed near $x = 0.3$. These phenomena are similar to those for alcohols + benzene [1], but the $H^E$ values for alcohols + chlorobenzene are about 170 J mol$^{-1}$ lower than those for alcohols + benzene. The behaviour of $H^E$ may be explained by the effects due to the molecular dissociation of both components and the formation of hydrogen bonds between unlike molecules. The chlorine atom in chlorobenzene decreases the electron density on the benzene ring because of its strong electron affinity and therefore decreases the interaction between alcohols and the benzene ring. On the other hand, the presence of the chlorine atom also increases the association between unlike molecules by the $OH \cdots Cl$ hydrogen bond. Comparing the benzene mixtures involved, the two effects together may be responsible for the lower $H^E$ values of the corresponding chlorobenzene mixtures. The positive values of $H^E$ for alcohols + chlorobenzene, however, suggest that the energy released in the formation of hydrogen bonds is less than that required to break associations present in the pure liquids.

The excess molar enthalpy curves of methanol, ethanol + aniline are sigmoid-shaped, in which the positive values are restricted to lower alcohol mole fractions. The $H^E$ values of methanol + aniline are more negative in magnitude and wider in alcohol mole fraction range than those of ethanol + aniline. For the other aniline mixtures, the $H^E$ values are all positive over the entire composition range. The maximum values are gradually shifted in the alcohol-rich direction and the mixing curves become symmetrical with increasing number of $-CH_2-$ groups in the alcohols. Considering the

TABLE 3

Coefficients $A_i$ for eqns. (1) and (2) and the standard deviations, $s$

| | $A_0$ | $A_1$ | $A_2$ | $A_3$ | $A_4$ | $A_5$ | $s$ |
|---|---|---|---|---|---|---|---|
| $x\mathrm{CH_3OH}+(1-x)\mathrm{C_6H_5NH_2}$ | −703.1 | 1037.2 | 188.9 | 642.6 | −884.9 | | 1.4 |
| $x\mathrm{CH_3OH}+(1-x)\mathrm{C_6H_5Cl}$ | 6760.4 | −366.9 | −33446.6 | 50251.0 | −22588.3 | | 2.5 |
| $x\mathrm{C_2H_5OH}+(1-x)\mathrm{C_6H_5NH_2}$ | 1401.9 | 1184.5 | 198.1 | −1149.9 | −715.2 | 1541.2 | 1.4 |
| $x\mathrm{C_2H_5OH}+(1-x)\mathrm{C_6H_5Cl}$ | 17110.4 | −49701.5 | 60579.8 | −27827.7 | | | 1.9 |
| $x\mathrm{C_3H_7OH}+(1-x)\mathrm{C_6H_5NH_2}$ | 3098.7 | 617.2 | 139.7 | 278.6 | | | 2.4 |
| $x\mathrm{C_3H_7OH}+(1-x)\mathrm{C_6H_5Cl}$ | 28866.9 | −123140.7 | 239053.1 | −215861.9 | 72539.6 | | 2.1 |
| $x\mathrm{C_5H_{11}OH}+(1-x)\mathrm{C_6H_5NH_2}$ | 4052.2 | 719.2 | 653.8 | 1273.9 | 244.9 | | 2.8 |
| $x\mathrm{C_5H_{11}OH}+(1-x)\mathrm{C_6H_5Cl}$ | 23867.0 | −85610.4 | 146631.7 | −119220.3 | 36378.7 | | 1.6 |
| $x\mathrm{C_6H_{13}OH}+(1-x)\mathrm{C_6H_5Cl}$ | 28692.5 | −120923.3 | 236129.6 | −214737.4 | 72959.0 | | 1.5 |

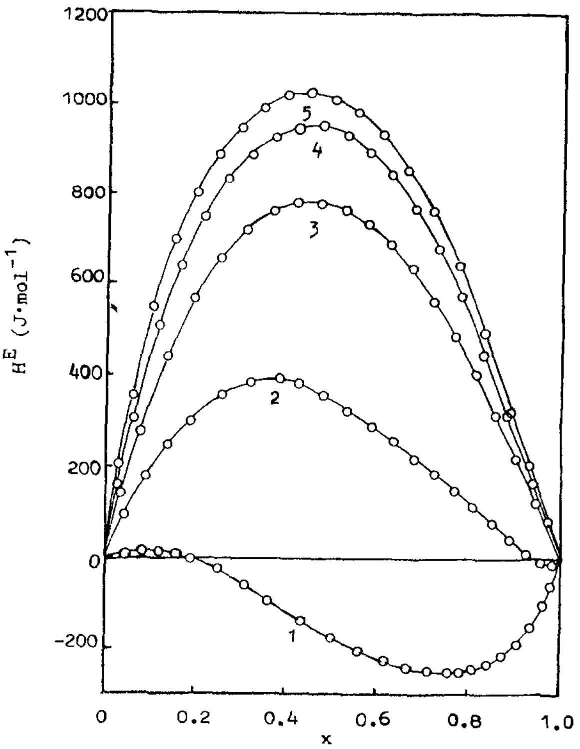
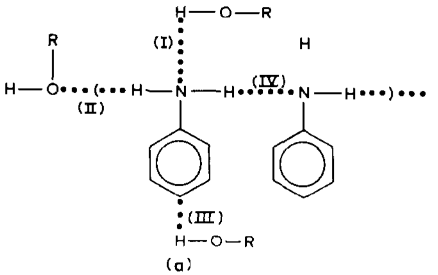
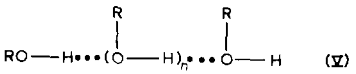


Fig. 1. Excess molar enthalpies of *n*-alcohols with aniline at 298.15 K. The curves were calculated from eqn. (1) with the coefficients from Table 3. o, Experimental data: 1, methanol; 2, ethanol; 3, *n*-propanol; 4, *n*-butanol; 5, *n*-pentanol;

structures and chemical properties of alcohols and aniline, there may be five kinds of hydrogen bond in the mixtures.



(a)



(b)

According to this assumption, the sign and magnitude of $H^E$ depend on the strength of the hydrogen bonds in pure alcohol and pure aniline and in their

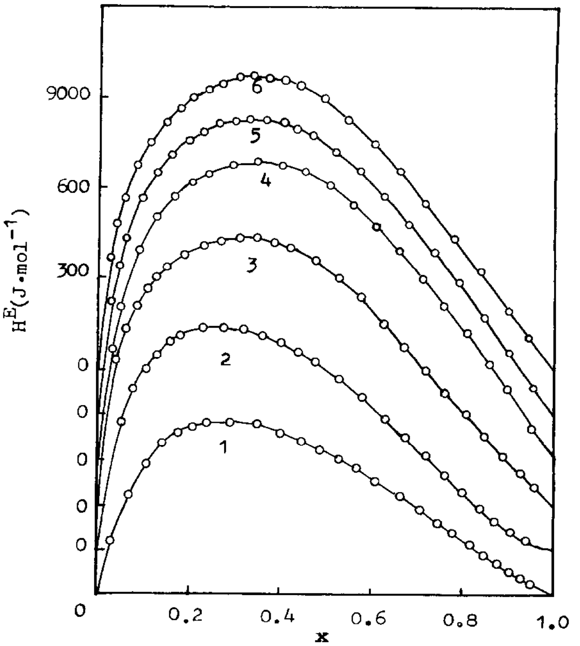


Fig. 2. Excess molar enthalpies of *n*-alcohols with chlorobenzene at 298.15 K. The curves were calculated from eqn. (2) with the coefficients from Table 3. o, Experimental data: 1, methanol; 2, ethanol; 3, *n*-propanol; 4, *n*-butanol; 5, *n*-pentanol; 6, *n*-hexanol.

mixtures. The negative values of $H^E$ suggested that the dominant effect in the mixing process is the strong exothermic association of hydrogen bonds between unlike molecules (bonds I, II, III).

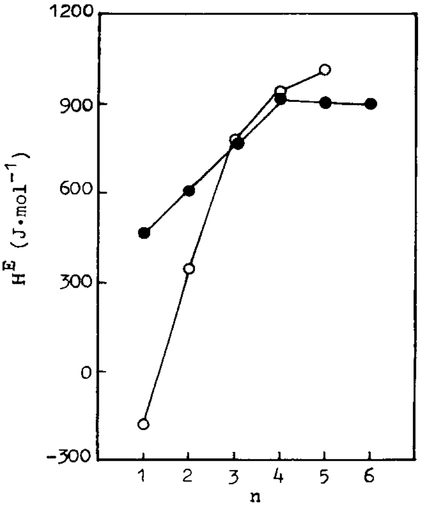


Fig. 3. Excess molar enthalpies of *n*-alcohols with aniline or chlorobenzene at $x = 0.5$ (298.15 K). ●, Chlorobenzene, o, aniline; $n$ = the number of carbon atoms in the alcohol.

It has been observed that the excess molar enthalpies of *n*-alcohols with cyclohexane [12], where there are no specific interactions between unlike molecules, are generally independent of the alcohol chain length. The same phenomenon also appears in the mixtures of an *n*-alcohol + an *n*-alkane. This indicates that various molecular interactions caused by increasing the number of $-CH_2-$ groups in the alcohol are essentially balanced in the mixing process. Hence, we consider that the alcohol chain length mainly influences the specific interactions between unlike molecules. This effect becomes more significant in mixtures containing a smaller alcohol. From Fig. 3, we can see that the difference between the $H^E$ values for methanol + aniline and ethanol + aniline is 526 J $mol^{-1}$ at $x = 0.5$, while that between *n*-butanol + aniline and *n*-pentanol + aniline is only 65 J $mol^{-1}$. Compared with aniline mixtures, the differences between the corresponding chlorobenzene mixtures are very much smaller. This indicates that specific interactions between alcohols and chlorobenzene are generally rather weaker.

## REFERENCES

1 J.P. Chao and M. Dai, Acta Phys. Chem. Sin., 2 (1986) 45.
2 M. Dai and J.P. Chao, Fluid Phase Equilibria, 23 (1985) 321
3 J.P. Chao and M. Dai, Thermochim. Acta, 123 (1988) 285.
4 J.P. Chao and M. Dai, J. Chem. Thermodyn., 21 (1989) 337.
5 J.P. Chao and M. Dai, J. Chem. Thermodyn., 21 (1989) 977.
6 J.P. Chao and M. Dai, J. Henan Acad. Sci., 3 (1984) 7.
7 J.P.E. Grolier, Thermochim. Acta, 16 (1976) 27.
8 J.A. Riddick and W.B. Bunger, Organic Solvents, Techniques of Chemistry, Vol. II, 3rd edn. Wiley, New York, 1970.
9 D.D. Deshpande and M.V. Pandya, Trans. Faraday Soc., 63 (1967) 2346.
10 G.L. Nicolaides and C.A. Eckert, J. Chem. Eng. Data, 23 (1978) 152.
11 I. Nagata and K. Tamura, J. Chem. Thermodyn., 20 (1988) 87.
12 J.P. Chao, Thesis, Henan Institute of Chemistry, 1986.