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EXCESS ENTHALPIES OF BINARY MIXTURES OF METHYL ACETATE WITH METHANOL, BUTAN-1-OL, HEXAN-1-OL, AND DECAN-1-OL

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SUMMARY

Molar excess enthalpies H^E of methyl acetate + methanol, + butan-1-ol, + hexan-1-ol, + decan-1-ol have been measured as a function of the liquid composition at 298 K using an isothermal flow calorimeter. H^E is positive in all cases ranging from 1000 J/mol (methanol) to 2400 J/mol (decan-1-ol) in the maximum of the H^E curve. Application of a theoretical model which accounts for hydrogen bonding effects as well as for non polar physical interactions indicates that the physical contribution to H^E is unusually large compared to the chemical contribution due to hydrogen bonding effects.

EXPERIMENTAL

Flow calorimetry has become a well established method for determining heats of mixing of liquids. A Tronac 1250 calorimeter originally designed for titration calorimetry has been used in a modified version which allows to operate the apparatus as a flow calorimeter (refs. 1,2). Fig. 1 shows schematically the calorimetric cell consisting of a cylindric vessel which is immersed in a large external water bath where the temperature is controlled to within $\pm 0.5\cdot 10^{-4}$ K. Two precision burets (PB) deliver continuously the two liquid components through tubings at constant flow rates $\dot{v}_1$ and $\dot{v}_2$. The liquids are mixed in the calorimetric cell and the mixture leaves the cell after having exchanged its heat of mixing with the water bath inside the cell. The water is used as a heat conducting medium. At the bottom of the vessel a peltier cooler (PC) removes energy from the water at a constant rate. A controlled heater (CH) compensates for this energy and additionally for the energy librated or absorbed by the mixing process maintaining the water in the vessel at constant temperature which is identical with the reference temperature in the external water bath. The change of the heating power of CH during and before or after a measurement run is a direct measure for the heat of mixing. Exothermic as well as endothermic processes can be registered by this method. Mixtures of different compositions can be studied by changing the ratio of the flow rates $\dot{v}_1$ and $\dot{v}_2$.

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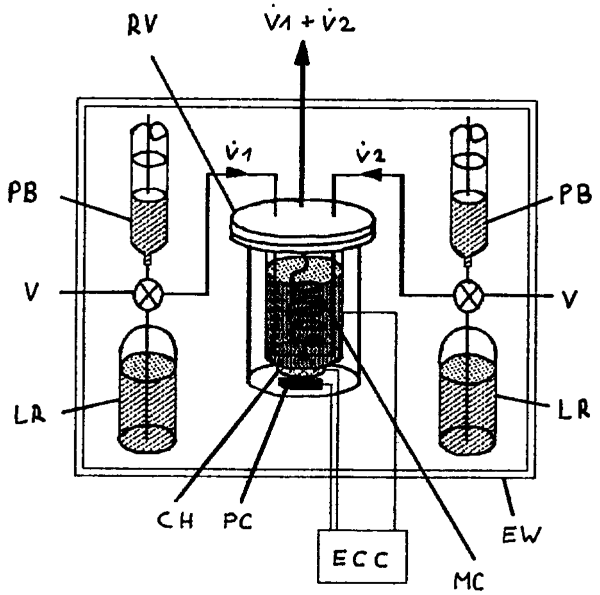


Fig. 1. Schematic representation of the calorimeter. RV=reaction vessel (calorimetric cell), PB=precision burets, V=valve, LR=liquid reservoirs, CH=controlled heater, PC=peltier cooler, ECC=electronic control ciruit, MC=mixing coil, EW=external water bath, $\dot{v}_1$, $\dot{v}_2$ =flow rates of the pure liquids.

RESULTS AND DISCUSSION

In table 1 the experimental results are listed for H^E as a function of the mole fraction x_A of the alkanol. Fig. 2 shows the graphical representation of the results. H^E is large and positive showing increasing values with increasing chain length of the alkanol.

An attempt has been made to distinguish between a so-called chemical contribution to H^E which accounts for the associational effect due to hydrogen bondings between alkanol-alkanol and alkanol-ester molecules and a so-called physical contribution to H^E which arises from different non polar intermolecular forces between the molecules in the mixture. The expression for the chemical contribution is based on the assumption that the alkanol molecules form linear chainlike associated species described by an association constant K_A which is independent of the chain length. Details of this model are given elsewhere (ref. 3). This model has been extended to the case where the second component is not an inert solvent but a molecule such as methyl acetate which is able to act as a proton acceptor for alcohol molecules. The chemical contribution H^E_{chem} to H^E is given by

$$H^E_{chem} = x_A \cdot \Delta h^*_A \cdot K_A \cdot (\varphi_{A1} - \varphi^0_{A1}) + x_A \cdot \Delta h^*_{AB} \cdot K_{AB} \cdot \frac{\varphi_{B1} \cdot (1 - K_A \cdot \varphi_{A1})}{V^*_B / V^*_B + K_{AB} \cdot \varphi_{B1}} \qquad (1)$$

Details of the derivation of eq. (1) are given in ref. 4. Δh^*_A and Δh^*_{AB} are the reaction enthalpy of the hydrogen bonding of alkanol with alkanol and of alkanol with acetate respectively. K_{AB} is the association constant of alkanol (A) and acetate (B). φ_{A1} and φ_{B1} are the volume fractions of the monomeric species A and B in the mixture and φ^0_{A1} is the volume fraction of monomeric A in the pure alkanol. V^*_A and V^*_B are the so-called hard core volumes of the monomers A and B.

TABLE 1

Experimental excess enthalpy H^E of some alkanol + methyl acetate binary mixtures.

x_A	H^E(J/mol)	x_A	H^E(J/mol)	x_A	H^E(J/mol)	x_A	H^E(J/mol)
x_A CH_3OH + $(1-x_A)$ CH_3COOCH_3							
0.081	419	0.305	972	0.540	1006	0.814	571
0.105	502	0.370	1024	0.622	911	0.867	431
0.180	753	0.468	1028	0.686	824		
0.227	857	0.485	1019	0.766	674		
x_A C_4H_9OH + $(1-x_A)$ CH_3COOCH_3							
0.089	711	0.281	1590	0.511	1822	0.794	1191
0.115	883	0.343	1738	0.592	1770	0.853	940
0.163	1151	0.438	1835	0.663	1650	0.886	751
0.207	1336	0.494	1855	0.743	1404		
x_A $C_6H_{13}OH$ + $(1-x_A)$ CH_3COOCH_3							
0.067	651	0.223	1619	0.515	2066	0.810	1286
0.087	816	0.277	1820	0.587	2004	0.850	1086
0.125	1099	0.365	2012	0.681	1821	0.914	663
0.160	1307	0.415	2067	0.739	1646		
x_A $C_{10}H_{21}OH$ + $(1-x_A)$ CH_3COOCH_3							
0.045	601	0.200	1844	0.412	2411	0.788	1544
0.059	769	0.258	2106	0.483	2411	0.903	717
0.085	1055	0.272	2104	0.582	2304		
0.111	1288	0.319	2258	0.650	2148		
0.158	1609	0.333	2285	0.736	1820		

The physical contribution H^E_{phys} is identical with the expression for H^E obtained from Flory's free volume theory of non polar mixtures :

$$H^E_{phys} = (x_A \cdot V^*_A + x_B \cdot V^*_B) \cdot \left[\frac{\Phi_A \cdot p^*_A}{\tilde{v}_A} + \frac{\Phi_B \cdot p^*_B}{\tilde{v}_B} - \frac{p^*_M}{\tilde{v}_M} \right] \qquad (2)$$

In eq. (2) Φ_A and Φ_B are the stoichiometric hard core volume fractions of A and B respectively. $\tilde{v}_A$ and $\tilde{v}_B$ are the reduced molar volumes and p_A^* and p_B^* are the reduction parameters for the pressure in Flory's equation of state of the pure liquids. p_M^* and $\tilde{v}_M$ are the corresponding values for the mixture. They are functions of the mole fraction $x_A=1-x_B$ of the mixture. Additionally p_M^* depends on a parameter X_{AB} which characterizes the difference of non polar intermolecular energies of A–A, B–B, and A–B. X_{AB} is an adjustable parameter. V_A^* , V_B^* , p_A^* , and p_B^* are obtained by fitting Flory's equation of state to experimental PVT–data of the pure liquids.

The expression of H^E for describing the behavior of alkanol + acetate mixtures i given by

$$H^E = H^E_{chem} + H^E_{phys} \tag{3}$$

The number of adjustable parameters appearing in eq. (3) is reduced in the following way. X_{AB} is determined by adjusting H^E_{phys} to experimental data of methyl acetate +

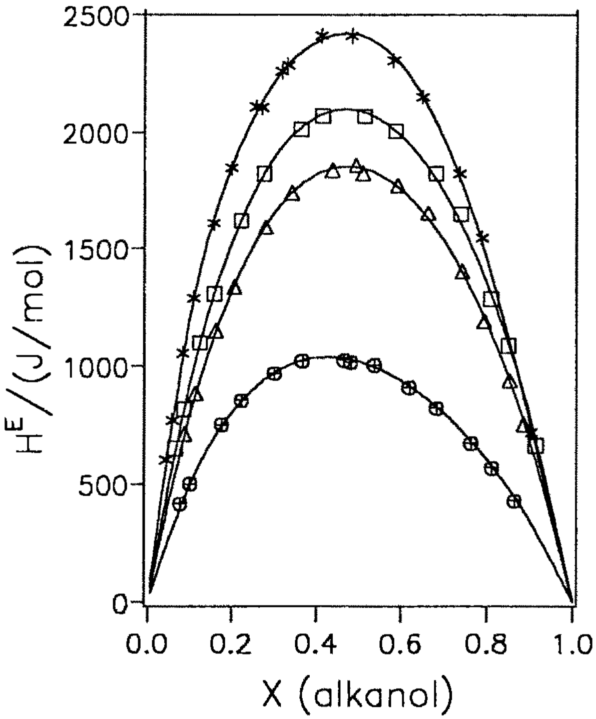
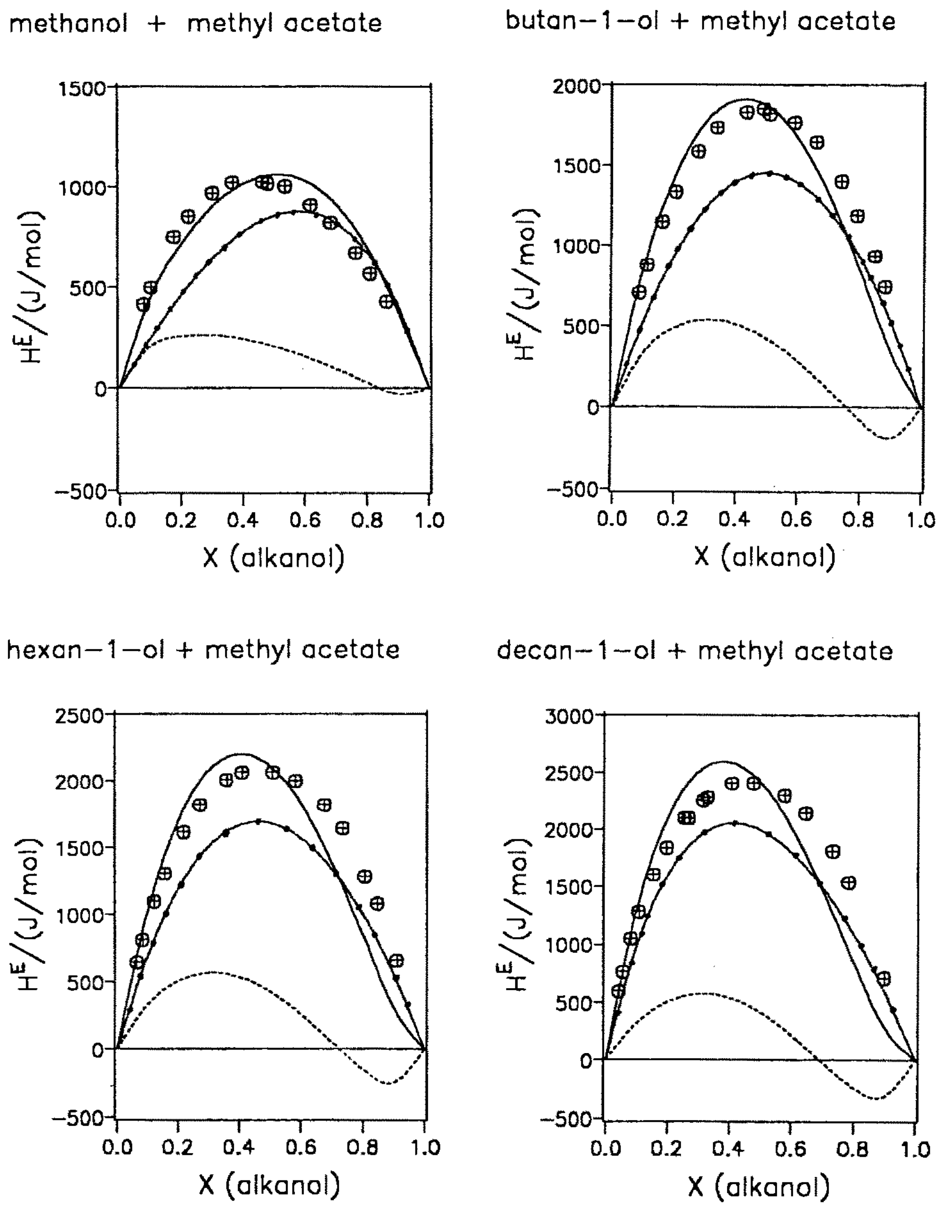


Fig. 2. Graphical representation of experimental H^E of alkanol + methyl acetate mixtures. methyl acetate + methanol ⊕, + butan-1-ol △, + hexan-1-ol □, + decan-1-ol ✱ .



methanol + methyl acetate

butan-1-ol + methyl acetate

hexan-1-ol + methyl acetate

decan-1-ol + methyl acetate

Fig. 3. Experimental H^E data compared to theoretical H^E curves. H^E_{chem} according to eq. (1) ---, H^E_{phys} according to eq. (2) —•—•—, H^E_{total} according to eq. (3) ——, experimental data ⊕ .

alkane mixtures (ref. 5). K_A and Δh^*_A are taken from literature where these parameters have been adjusted to alkanol + alkane mixtures (ref. 3). Δh^*_{AB} has been taken from data in the literature obtained by a UV-spectroscopic method applied to Phenol + methyl acetate mixtures (ref. 6). K_{AB} is the only parameter which is adjustable to H^E of methyl acetate + alkanol systems. All parameters used in this work are given in table 2. The results of fitting eq. (3) to H^E are shown in Fig. 3. H^E_{chem} is a S-shaped curve and H^E_{phys} is the dominating contribution to H^E . The symmetry of the experimental H^E-curve is not represented sufficiently by the theoretical H^E-curve. The large contribution of H^E_{phys} to H^E arises from the strong intermolecular interactions between the methyl acetate molecules which have to be separated upon mixing. These interactions are by no means non polar interactions as required for applicating Flory's theory. The methyl acetate molecule has a remarkable dipole moment. The reason for the discrepancy in the symmetry between experimental and theoretical H^E probably arises from the fact that H^E_{phys} is based on the assumption of a random arrangement of the molecules and associated species in the mixture. This assumption is not justified when the physical interactions have a too polar character.

TABLE 2

Parameters used in eqs. (1-3) for calculating H^E.

system: methyl acetate +	K_A (-)	K_{AB} (-)	Δh^*_A (kJ/mol)	Δh^*_{AB} (kJ/mol)	χ_{12} (J/cm^{-3})	temperature (K)
methanol	985	18	-25.1	-18.8	79.3	298
butan-1-ol	175	55				
hexan-1-ol	120	63				
decan-1-ol	88	72				

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