

## New applications of the ERAS model. Thermodynamics of amine+alkane and alcohol+ amine mixtures

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**Abstract**—The ERAS model (extended real associated solution model) originally developed for describing alcohol/hydrocarbon mixing properties has been applied to amine/hydrocarbon mixtures. A generalized version is presented which also allows a description of excess properties of mixtures consisting of two associating components provided one of these components shows a weak self-association. Binary amine/alcohol systems have been studied involving methanol, ethanol, 1-propanol, and 1-butanol as alcohols and butylamine, diethylamine and triethylamine as amines. Values of the cross hydrogen bonding energy between -32 kJ/mol and -45 kJ/mol have been determined exceeding significantly the corresponding values of the self-association of alcohols (-25.1 kJ/mol) and amines (-8.5 kJ/mol and -13.2 kJ/mol). Hydrogen bonding volumes of about -15 cm<sup>3</sup>/mol have been obtained for the cross interaction from the model adjustment compared to -5.6 cm<sup>3</sup>/mol and -2.8 cm<sup>3</sup>/mol (-4.7 cm<sup>3</sup>/mol) found for self-association of alcohols and amines respectively.

### INTRODUCTION

The excess enthalpy  $H^E$  and the excess volume  $V^E$  of liquid alcohol/amine mixtures belong to the excess functions with the strongest negative values found for organic mixtures in the literature. Even though this fact has been known for a couple of years it has not gained much interest so far in literature dealing with thermodynamic models of mixtures based on a molecular concept. In this paper a molecular model is presented which allows not only a description of the special behavior of these mixtures but also sheds some light on the physical background in terms of intermolecular interactions. It is well known that alcohol as well as amine molecules have a pronounced tendency to form associated species due to hydrogen bonding effects. A consistent molecular model which accounts for the self-association of alcohols in the pure state and in alcohol + alkane mixtures has been developed independently by Renon and Prausnitz (ref. 1) and by Kehiaian and Treszczanowicz (ref. 2). This model is called the real associated solution model. However, it is based on a rigid lattice approach and therefore is not able to describe  $V^E$  and related properties. An extended version of this association theory is the so-called ERAS model (extended real associated solution model) (ref. 3). It combines the associated solution model with an equation of state developed by Flory and coworkers (refs. 4 and 5). The ERAS model has successfully been applied describing simultaneously  $H^E$  and  $V^E$  of alcohol + alkane mixtures (ref. 3) as well as activity coefficients (ref. 6) and apparent molar volumes (ref. 7). All association concepts mentioned above have some simplifying assumptions in common. Only a consecutive linear association of alcohol molecules A is assumed which is described by a chemical equilibrium constant  $K_A$  being independent of the chain-length  $i$  of the associated species  $A_i$ :



No cyclic species are taken into account. This association model is a good approach for the mechanism occurring in pure alcohols plus an inert solvent such as saturated hydrocarbons. It can

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also be used to describe the thermodynamic properties of amines and amine/hydrocarbon mixtures. According to Flory's fundamental work (ref. 8) the association constant  $K_A$  is a true constant depending only on temperature if it is defined by the following equation:

$$K_A = \frac{c_{A_i}}{c_{A_{i+1}} \cdot c_{A_1}} \cdot \frac{1}{V_{A_1}^*} = K_{A0} \cdot \exp \left\{ -\frac{\Delta h_A^*}{R} \cdot \left[ \frac{1}{T} - \frac{1}{T_0} \right] \right\} \quad (2)$$

$c_{A_i}$ ,  $c_{A_{i+1}}$ , and  $c_{A_1}$  are the molar concentrations of  $A_i$ ,  $A_{i+1}$ , and  $A_1$  respectively.  $V_{A_1}^*$  is the hard core volume of the monomeric alcohol and  $\Delta h_A^*$  is the hydrogen bonding energy. The application of the ERAS model to alcohol/amine systems requires an extension in which cross associated species are also considered. It is a difficult task to account for all possible combinations of distinguishable species consisting of  $i$  alcohol and  $j$  amine molecules in an alcohol/amine mixture. We restrict the extension of the ERAS model to the assumption that only "block copolymers"  $A_i B_j$  with two blocks of length  $i$  and  $j$  are present in a cross associated multimer of chain-length  $i + j$  according to the equation:



where all combinations of numbers  $i$  and  $j$  are possible. A thermodynamically consistent theory confined to this restriction has been published by Nath and Bender (ref. 9). We call it the two-block model. If the self-association of amines is small compared to that of alcohols ( $K_B \ll K_A$ ) the two-block model will approach the special case where  $j \cong 1$ . This means that almost only  $A_i B_1$  species appear as cross multimers in the solution. As shown in the following section it turns out that the  $K$ -values of amines are indeed much smaller than those of alcohols suggesting that the two-block model can be considered to be a good approach in accounting for all essential cross associated multimers occurring in alcohol/amine mixtures.

## EXCESS FUNCTIONS

### A. Alcohol/alkane and amine/alkane mixtures

The derivation of the ERAS model starts with the partition function of a mixture of self-associating (A) and inert molecules (B). The details of its derivation are given elsewhere (ref. 3). The excess functions  $G^E$ ,  $H^E$  and  $V^E$  are split into a chemical (index c) and a physical contribution (index p). The following equations are obtained:

$$H^E = H_c^E + H_p^E \quad (4)$$

with

$$H_c^E = x_A \cdot K_A \cdot \Delta h_A^* \cdot (\varphi_{A_1} - \varphi_{A_1}^0) - x_A \cdot \frac{P_M^*}{V_M} \cdot K_A \cdot \Delta v_A^* \cdot (\varphi_{A_1} - \varphi_{A_1}^0) \quad (5)$$

$$H_p^E = (V_A^* \cdot x_A + V_B^* \cdot x_B) \cdot \left[ \frac{\Phi_A \cdot P_A^*}{V_A} + \frac{\Phi_B \cdot P_B^*}{V_B} - \frac{P_M^*}{V_M} \right] \quad (6)$$

and

$$G^E = G_c^E + G_p^E \quad (7)$$

with

$$G_c^E = RT \cdot \left[ x_A \cdot \ln \frac{\varphi_{A_1}}{\varphi_{A_1}^0 \cdot x_A} + x_B \cdot \ln \frac{\Phi_B}{x_B} + K_A \cdot x_A \cdot (\varphi_{A_1} - \varphi_{A_1}^0) \right] \quad (8)$$

$$G_p^E = H_p^E - T \cdot (V_A^* \cdot x_A + V_B^* \cdot x_B) \cdot \left[ \Theta_B \cdot \Phi_A \cdot Q_{AB} - 3 \cdot \Phi_A \cdot \frac{P_A^*}{T_A^*} \cdot \ln \left[ \frac{\frac{\sqrt[3]{V_A} - 1}{\sqrt[3]{V_M} - 1}}{\frac{\sqrt[3]{V_B} - 1}{\sqrt[3]{V_M} - 1}} \right] \right. \\ \left. - 3 \cdot \Phi_B \cdot \frac{P_B^*}{T_B^*} \cdot \ln \left[ \frac{\frac{\sqrt[3]{V_B} - 1}{\sqrt[3]{V_M} - 1}}{\frac{\sqrt[3]{V_A} - 1}{\sqrt[3]{V_M} - 1}} \right] \right] \quad (9)$$

The excess volume  $V^E$  is given by

$$V^E = V_c^E + V_p^E \quad (10)$$

with

$$V_c^E = x_A \cdot \tilde{v}_M^* \cdot \Delta v_A^* \cdot K_A \cdot (\varphi_{A1} - \varphi_{A1}^0) \quad (11)$$

$$V_p^E = (V_A^* \cdot x_A + V_B^* \cdot x_B) \cdot (\tilde{v}_M - \Phi_A \cdot \tilde{v}_A - \Phi_B \cdot \tilde{v}_B) \quad (12)$$

In eq. (4-12)  $x_A$  is the mole fraction of the alcohol or amine and  $x_B = 1 - x_A$  is the mole fraction of the inert solvent (hydrocarbon). Other concentration measures are the hard core volume fractions  $\Phi_A$  and  $\Phi_B$ :

$$\Phi_A = 1 - \Phi_B = \frac{x_A \cdot V_A^*}{x_A \cdot V_A^* + x_B \cdot V_B^*} \quad (13)$$

and the surface fractions  $\Theta_A$  and  $\Theta_B$ :

$$\Theta_B = 1 - \Theta_A = \frac{s_{AB} \cdot \Phi_B}{\Phi_A + s_{AB} \cdot \Phi_B} \quad (14)$$

where  $V_A^*$  and  $V_B^*$  are the hard core volumes of A (alcohol or amine) and B (hydrocarbon).  $s_{AB}$  is the surface to volume ratio of A to B which can be calculated from molecular geometry data using Bondi's method (ref. 10).  $K_A$  and  $\Delta h_A^*$  are the equilibrium constant and the reaction energy of hydrogen bonding as defined by eq. (2).  $\Delta v_A^*$  is the reaction volume of the hydrogen bonding.  $\varphi_{A1}$  and  $\varphi_{A1}^0$  are the volume fractions of the monomeric alcohol or amine respectively.  $\varphi_{A1}$  depends on  $\Phi_A$  and is connected to  $K_A$ :

$$\varphi_{A1} = \frac{2 \cdot K_A \cdot \Phi_A + 1 - \sqrt{4 \cdot K_A \cdot \Phi_A + 1}}{2 \cdot K_A^2 \cdot \Phi_A} \quad (15)$$

If  $\Phi_A = 1$  then  $\varphi_{A1}$  becomes  $\varphi_{A1}^0$ .  $V_i^*$ ,  $p_i^*$ , and  $T_i^*$  are reduction parameters for the molar volume, the pressure, and the temperature respectively.  $\tilde{v}_i = V_i/V_i^*$  is the reduced volume of the pure component  $i$  and  $\tilde{v}_M$  is the corresponding value for the mixture defined by  $\tilde{v}_M = V_M/(V_A^* \cdot x_A + V_B^* \cdot x_B)$  where  $V_M$  is the molar volume of the mixture.  $p_M^*$  is the reduction parameter of the pressure in the mixture. It is defined by the following equation:

$$p_M^* = p_A^* \cdot \Phi_A + p_B^* \cdot \Phi_B - \Phi_A \cdot \Theta_B \cdot X_{AB} \quad (16)$$

$X_{AB}$  is an adjustable parameter. Reduction parameters  $V_i^*$ ,  $p_i^*$ , and  $T_i^*$  are defined for pure substances using experimental data of the thermal expansion coefficient  $\alpha_i = (d \ln V_i / dT)_p$ , the compressibility  $\kappa_i = -(d \ln V_i / dp)_T$ , and the molar volume  $V_i$ . Adjustable parameters appearing in eqs. (4-12) have to be fixed properly before  $G^E$ ,  $H^E$ , and  $V^E$  can be calculated as functions of the mixture composition. Details of this procedure are given elsewhere (ref. 3). In applying eqs. (4-12) to alcohol/alkane mixtures it has been found that  $\Delta h_A^* = -25.1$  kJ/mol and  $v_A^* = -5.6$  cm<sup>3</sup>/mol are constant values valid for all alcohols. For  $K_A$  generally adopted values have been used which are different for each alcohol.  $K_A$ -values are listed in Table 1 together with other ERAS model parameters of alcohols, amines and alkanes. There remain only two parameters,  $X_{AB}$  and  $Q_{AB}$ , which have to be adjusted to excess properties of alcohol/alkane mixtures.  $X_{AB}$  is the energetic interaction parameter characterizing the difference of dispersive intermolecular interactions between A and B.  $Q_{AB}$  appears only in  $G^E$  (eq. 9), it characterizes the entropic contribution to the difference of intermolecular interactions. The following procedure is used for describing  $G^E$ ,  $H^E$ , and  $V^E$  simultaneously in alcohol/alkane mixtures. First  $X_{AB}$  is adjusted to experimental data of  $H^E$ , secondly  $Q_{AB}$  is adjusted to experimental data of  $G^E$  with fixed value of  $X_{AB}$ .  $V^E$  contains no additional parameter to be adjusted to  $V^E$  experiments.  $V^E$  calculated by eq. (10) is a purely predicted excess function. The progress made by introducing the ERAS model lies in its ability of predicting  $V^E$  of alcohol/alkane mixtures in a good agreement with experimental data. Many examples are given in literature (refs. 3 and 7). Figures 1 and 2 show selected results of the systems 1-octanol/nonane, 1-decanol/nonane, 1-hexanol/hexane, and 1-hexanol/decane. The S-shaped curves result from the counteracting contributions  $V_c^E$  and  $V_p^E$  to  $V^E$ .

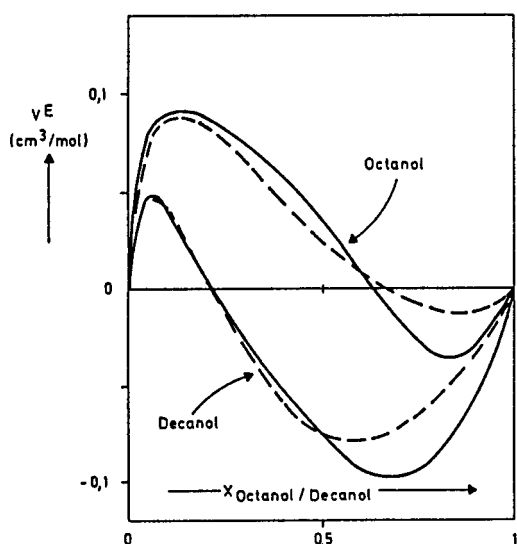


Fig. 1 Excess volumes of 1-Octanol/Nonane and 1-Decanol/Nonane at 298.15 K.  
 - - - - experiments (ref. 3)  
 ——— ERAS model (ref. 3)

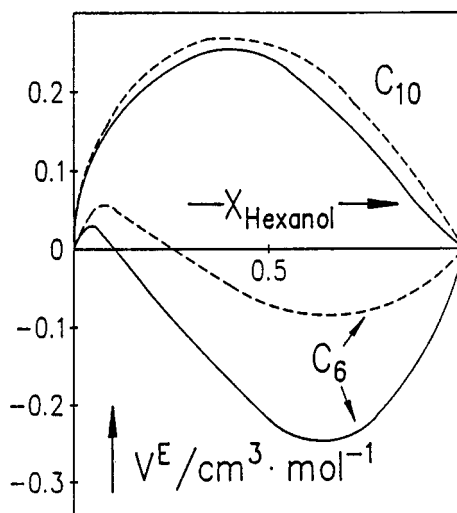


Fig. 2 Excess volumes of 1-Hexanol/Decane and 1-Hexanol/Hexane at 298.15 K.  
 - - - - experiments (ref. 7)  
 ——— ERAS model (ref. 7)

$V_c^E$  and  $V_p^E$  are usually different in sign and symmetry. In this paper some new results of applications of the ERAS model to amine/alkane systems are presented. In Fig. 3 results of  $H^E$ ,  $G^E$ , and  $V^E$  are compared to experimental data taken from literature (refs. 11-13). Values of  $K_A$ ,  $\Delta h_A^*$ , and  $X_{AB}$  have been obtained by adjusting them simultaneously to  $H^E$  and  $G^E$ .  $X_{AB}$  is allowed to take values between 2 and 14 J/cm<sup>3</sup>.  $\Delta v_A^*$  has been adjusted to  $V^E$  with fixed values of  $K_A$ ,  $\Delta h_A^*$  and  $X_{AB}$ . All excess functions are positive.  $H^E$  and  $G^E$  are dominated by the chemical contributions whereas both,  $V_c^E$  and  $V_p^E$ , contribute to similar extents to  $V^E$ . Results of the adjusted model parameters are given in Table 1 and 2. Compared to alcohol/alkane systems  $\Delta h_A^*$  and  $K_A$  are much smaller for amines, the hydrogen bonding N-H...N is weaker than the O-H...O bonding. Also  $\Delta v_A^*$  is smaller for amines than for alcohols.

## B. Alcohol/amine mixtures

The ERAS model is extended to mixtures consisting of two associating components such as alcohol/amine systems. The two-block model introduced by Nath and Bender (ref. 9) has been incorporated into the ERAS concept for describing the chemical contribution of the excess properties. It is obvious from the results shown in Table 1 that  $K_{\text{amine}} \ll K_{\text{alcohol}}$ . This relation justifies the application of the two-block approach to amine/alcohol systems as discussed above. The generalized formulas for the excess functions of the ERAS model extended to the two-block approach of cross association are given by the following equations:

$$G^E = G_c^E + G_p^E \quad (17)$$

with

$$G_c^E = RT \cdot \left[ x_A \cdot \ln \frac{\varphi_{A1}}{\varphi_{A1}^0 \cdot x_A} + x_B \cdot \ln \frac{\varphi_{B1}}{\varphi_{B1}^0 \cdot x_B} - \frac{V_M}{V} + x_A \cdot \frac{V_A}{V_A^0} + x_B \cdot \frac{V_B}{V_B^0} \right] \quad (18)$$

$$G_p^E = -T \cdot (V_A^* \cdot x_A + V_B^* \cdot x_B) \cdot \left[ \Theta_B \cdot \Phi_A \cdot Q_{AB} - 3 \cdot \Phi_A \cdot \frac{P_A^*}{T_A^*} \cdot \ln \left[ \frac{\tilde{V}_A^{1/3} - 1}{\tilde{V}_M^{1/3} - 1} \right] - 3 \cdot \Phi_A \cdot \frac{P_B^*}{T_B^*} \cdot \ln \left[ \frac{\tilde{V}_B^{1/3} - 1}{\tilde{V}_B^{1/3} - 1} \right] \right] + H_p^E \quad (19)$$

Table 1. ERAS model parameters of 1-Alkanols, Amines, and Alkanes obtained from PVT-data of the pure substances and from 1-Alkanol/Alkane or Amine/Alkane mixture properties.

	T	K	p*	V <sub>Mol</sub>	V*	$\alpha$	$\kappa$	$\Delta h^*$	$\Delta v^*$
	[K]		[J/cm <sup>3</sup> ]	[cm <sup>3</sup> /mol]	[cm <sup>3</sup> /mol]	[10 <sup>-4</sup> /K]	[10 <sup>-4</sup> /MPa]	[kJ/mol]	[cm <sup>3</sup> /mol]
Methanol	298.15	986	423.1	40.72	32.1	11.89	12.48	-25.1	-5.6
Ethanol	293.15	377	422.7	58.37	46.8	11.2	11.05	-25.1	-5.6
	298.15	317	411.8	58.66	46.9	11.2	11.53	-25.1	-5.6
	303.15	267	403.9	58.99	47.1	11.2	11.95	-25.1	-5.6
	307.95	230	393.6	59.30	47.2	11.2	12.45	-25.1	-5.6
Propanol	293.15	226	428.4	74.74	60.9	10.2	9.55	-25.1	-5.6
	298.15	197	414.1	75.12	61.1	10.2	10.06	-25.1	-5.6
	313.15	121	390.2	76.72	62.0	10.2	11.20	-25.1	-5.6
Butanol	298.15	175	396.7	91.98	75.7	9.32	9.42	-25.1	-5.6
	313.15	108	392.9	92.77	75.7	9.50	10.25	-25.1	-5.6
Hexanol	298.15	120	405.0	125.26	104.3	8.58	8.36	-25.1	-5.6
Octanol	298.15	89	439.0	158.34	131.7	8.52	7.77	-25.1	-5.6
Decanol	298.15	88	446.0	191.57	160.1	8.18	7.33	-25.1	-5.6
Diethylamine	293.15	0.89	518.2	103.77	78.6	15.2	13.99	-8.5	-4.7
	298.15	0.84	511.3	104.57	78.8	15.3	14.71	-8.5	-4.7
	303.15	0.79	503.8	105.37	79.0	15.4	15.49	-8.5	-4.7
	308.15	0.75	495.0	106.18	79.2	15.5	16.33	-8.5	-4.7
Triethylamine	293.15	0.0	471.3	139.11	107.2	12.75	13.35	0.0	0.0
	298.15	0.0	467.6	140.01	107.4	12.85	13.92	0.0	0.0
	307.95	0.0	451.2	141.78	108.0	12.95	15.24	0.0	0.0
	313.15	0.0	447.0	142.72	108.1	13.1	15.99	0.0	0.0
Butylamine	298.15	0.96	374.6	99.77	77.5	13.1	15.90	-13.2	-2.8
	313.15	0.74	351.1	101.62	78.0	13.2	18.54	-13.2	-2.8
Hexane	298.15	0.0	421.4	131.57	99.5	13.9	17.2	0.0	0.0
Heptane	298.15	0.0	431.7	147.42	113.7	12.47	14.47	0.0	0.0
	303.15	0.0	411.1	149.28	114.1	12.7	16.3	0.0	0.0
Nonane	298.15	0.0	441.0	178.88	141.6	10.83	11.71	0.0	0.0
Decane	298.15	0.0	449.7	195.95	155.9	10.44	11.42	0.0	0.0

Table 2. ERAS model parameters characterizing mixture properties of Amine/Alkane and 1-Alkanol/Amine systems.

Systems	T	K <sub>AB</sub>	$\Delta h_{AB}^*$	$\Delta v_{AB}^*$	X <sub>AB</sub>	Q <sub>AB</sub>	Ref. of exp. data		
	[K]		[kJ/mol]	[cm <sup>3</sup> /mol]	[J/cm <sup>3</sup> ]	[J/(cm <sup>3</sup> ·K)]	H <sup>E</sup>	G <sup>E</sup>	V <sup>E</sup>
Diethylamine/Heptane	298.15	0	0	0	8.8	0.012	11	-	11
	308.15	0	0	0	8.8	0.012	-	11	-
Butylamine/Hexane	298.15	0	0	0	7.3	-	12	-	13
Methanol/Diethylamin	298.15	3663	-44.6	-15.2	11.2	0.220	14	19	24
Ethanol/Diethylamine	293.15	2258	-35.6	-14.0	12.9	-	15	-	27
	303.25	1394	-35.6	-14.0	12.9	0.035	-	20	-
Ethanol/Triethylamine	298.15	154	-32.4	-15.1	8.0	-	16	-	25
	307.95	101	-32.4	-15.1	8.0	0.091	-	20	-
Propanol/Triethylamine	293.15	125	-32.4	-15.2	6.9	0.110	-	21	-
	298.15	100	-32.4	-15.2	6.9	-	18	-	25
Butanol/Triethylamine	298.15	77	-32.4	-15.8	3.4	-	18	-	25
	313.15	41	-32.4	-15.8	3.4	0.100	-	23	-
Propanol/Butylamine	298.15	1162	-38.5	-10.1	11.8	-	17	-	26
	313.15	552	-38.5	-10.1	11.8	0.023	-	21	-

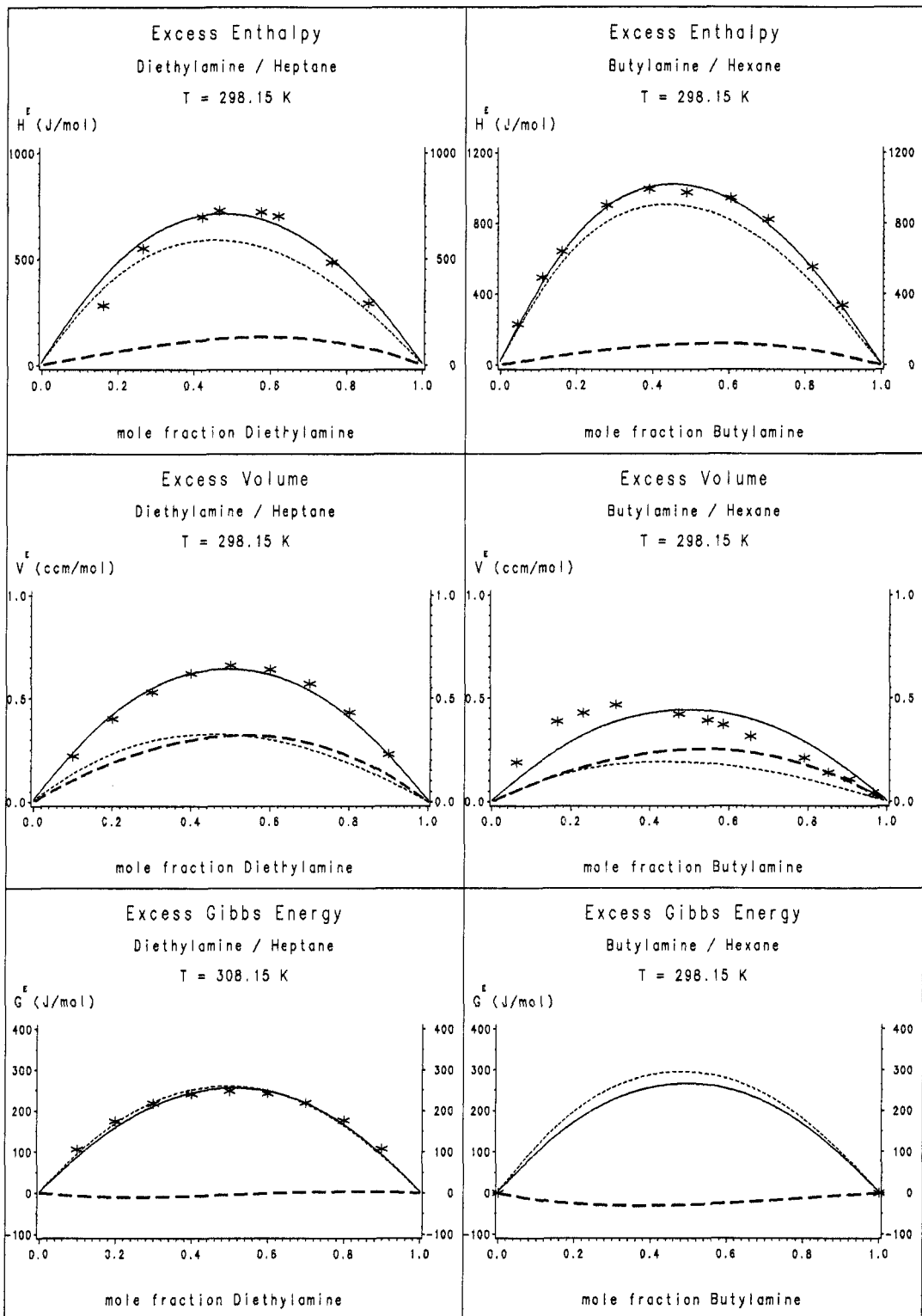


Fig. 3 Excess properties  $H^E$ ,  $V^E$ , and  $G^E$  of Amine/Alkane systems as indicated.  
 \* experiments (ref. 11-13)  
 — ERAS model calculations with parameters from Tables 1 and 2.  
 - - - chemical contribution to ERAS  
 - · - · physical contribution to ERAS

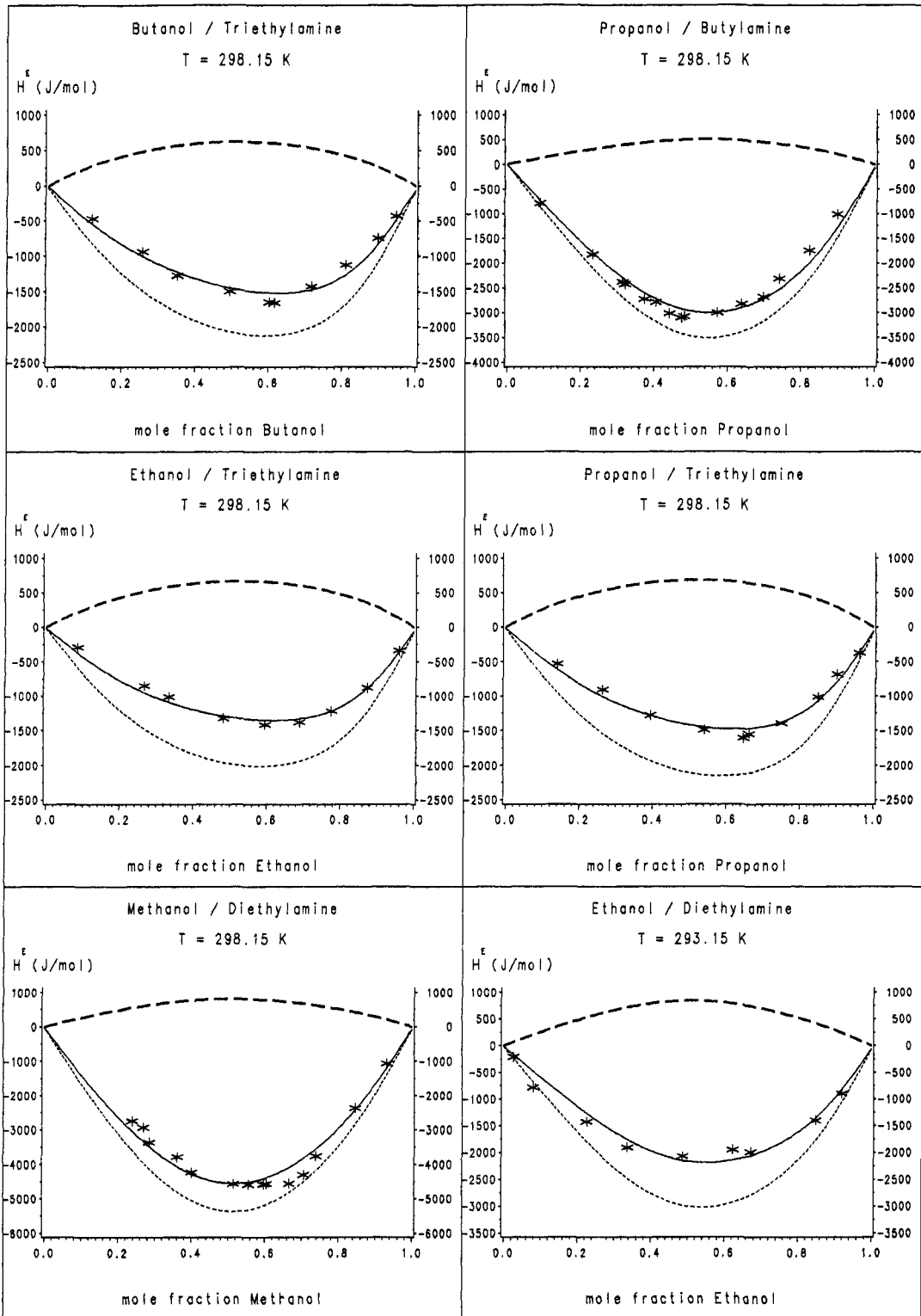


Fig. 4 Excess enthalpy  $H^E$  of 1-Alkanol/Amine systems.

- \* experiments (refs. 14-17)
- ERAS model calculations with parameters from Tables 1 and 2.
- - - - chemical contribution to ERAS
- · - · - physical contribution to ERAS

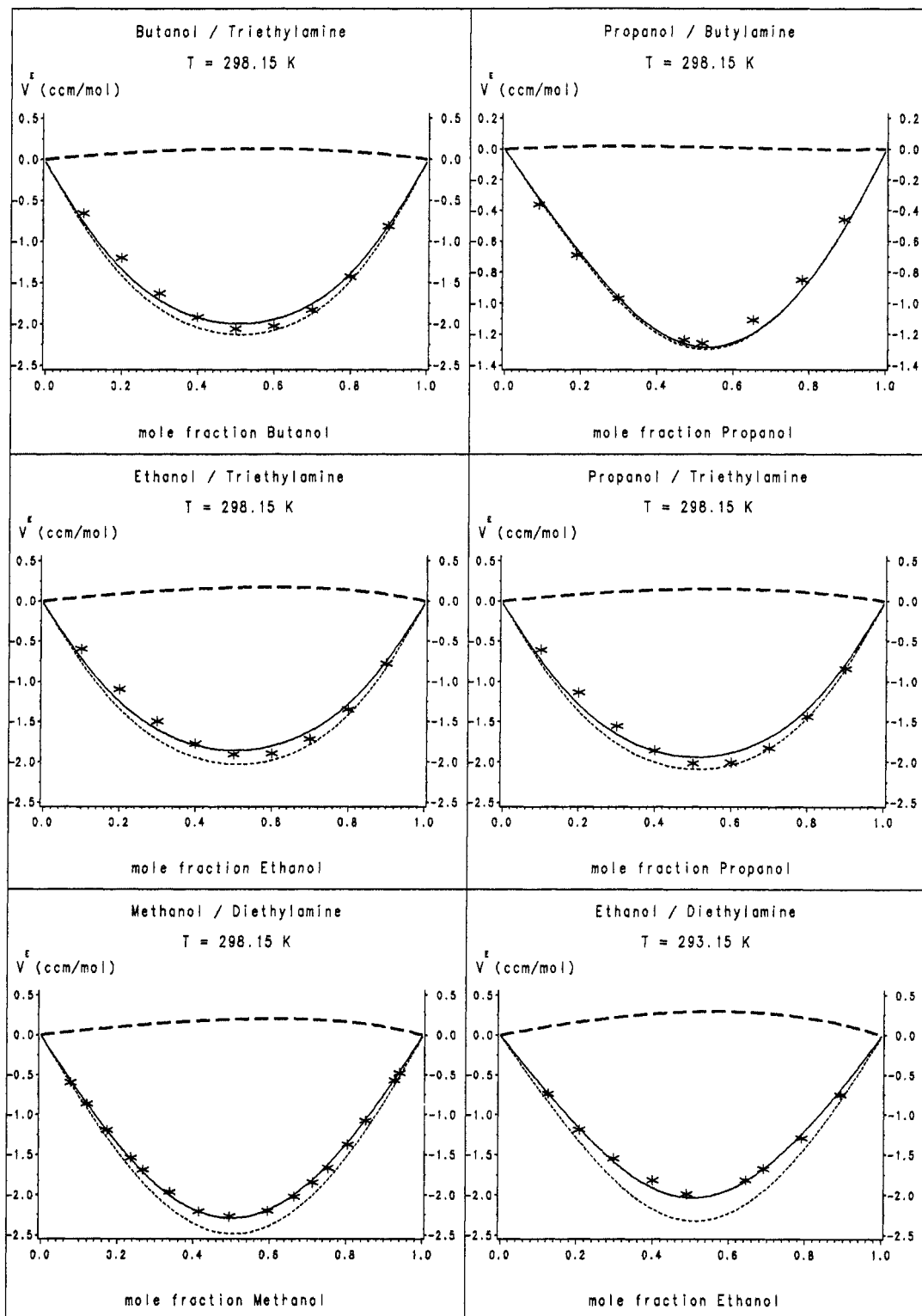


Fig. 5 Excess volume  $V^E$  of 1-Alkanol/Amine systems.

- \* experiments (refs. 11, 13, 24-27)
- ERAS model calculations with parameters from Tables 1 and 2.
- - - chemical contribution to ERAS
- · - · physical contribution to ERAS



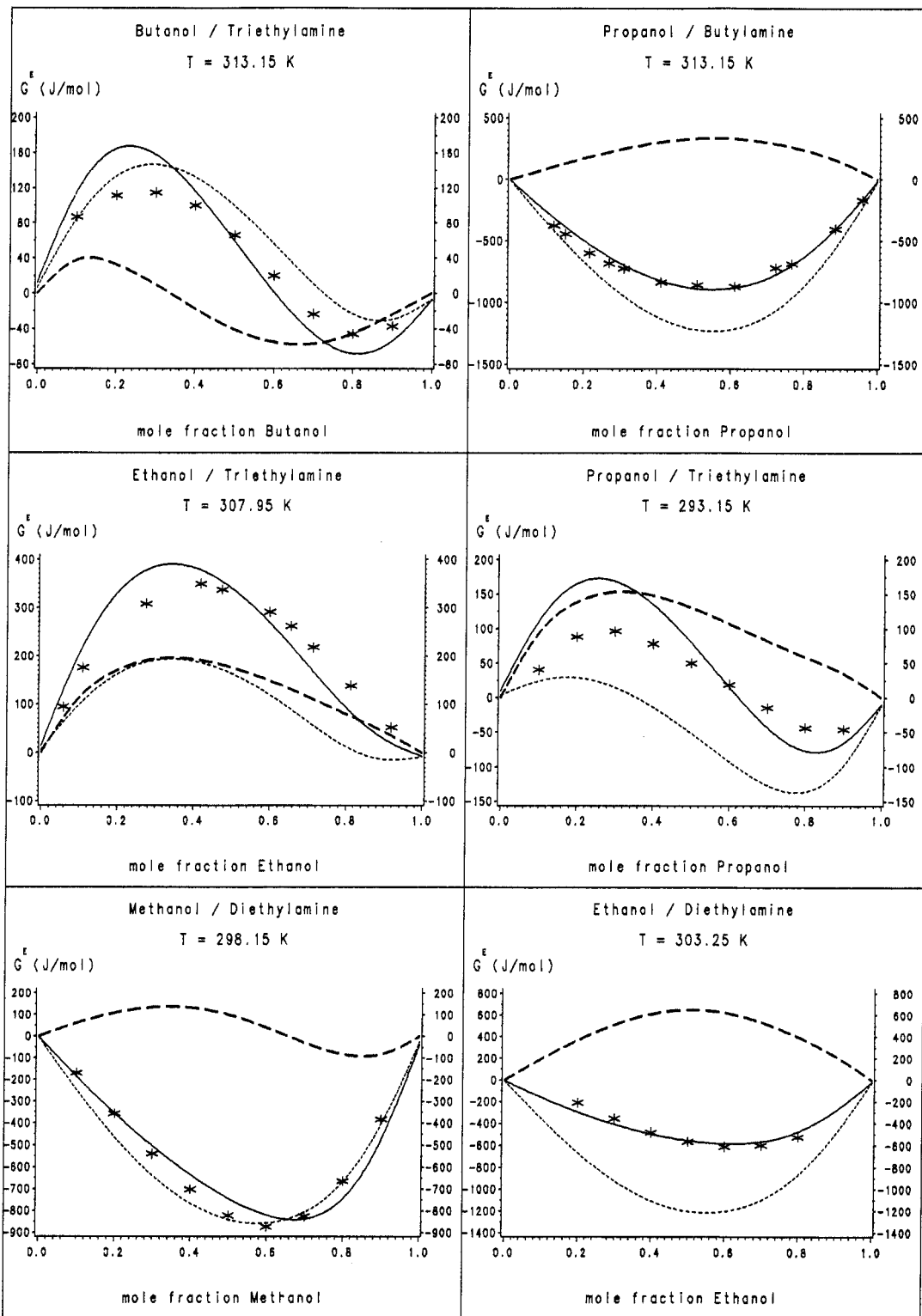


Fig. 6 Gibbs excess energy  $G^E$  of 1-Alkanol/Amine systems.

- \* experiments (refs. 11 and 19-23)
- ERAS model calculations with parameters from Tables 1 and 2.
- chemical contribution to ERAS
- · - · - physical contribution to ERAS

The meaning of the parameters appearing in eqs. (17-19) is the same as already discussed in section A.  $\varphi_{A1}$  and  $\varphi_{B1}$ , the volume fractions of the monomeric alcohol and amine species in the mixture are obtained from the following equations:

$$\Phi_A = \frac{\varphi_{A1}}{(1 - K_A \cdot \varphi_{A1})^2} \cdot \left( 1 + \frac{V_A \cdot K_{AB} \cdot \varphi_{B1}}{V_B \cdot (1 - K_B \cdot \varphi_{B1})} \right) \quad (20)$$

$$\Phi_B = \frac{\varphi_{B1}}{(1 - K_B \cdot \varphi_{B1})^2} \cdot \left( 1 + \frac{K_{AB} \cdot \varphi_{A1}}{(1 - K_A \cdot \varphi_{A1})} \right) \quad (21)$$

$$\frac{1}{V} = \frac{\varphi_{A1}}{V_A \cdot (1 - K_A \cdot \varphi_{A1})} + \frac{\varphi_{B1}}{V_B \cdot (1 - K_B \cdot \varphi_{B1})} + \frac{K_{AB} \cdot \varphi_{A1} \cdot \varphi_{B1}}{V_B \cdot (1 - K_A \cdot \varphi_{A1}) \cdot (1 - K_B \cdot \varphi_{B1})} \quad (22)$$

$1/V_A^0$  and  $1/V_B^0$  in eq. 18 are the values for  $1/V$  if  $\Phi_A = 1$  and  $\Phi_A = 0$  respectively.  $\varphi_{A1}$  and  $\varphi_{B1}$  are solved simultaneously from eq. (20) and (21) using a numerical method suitable for solving systems of nonlinear equations. The following expressions for  $H^E$  and  $V^E$  are obtained:

$$H^E = H_c^E + H_p^E \quad (23)$$

$$H_c^E = x_A \cdot K_A \cdot \Delta h_A^* \cdot (\varphi_{A1} - \varphi_{A1}^0) + x_B \cdot K_B \cdot \Delta h_B^* \cdot (\varphi_{B1} - \varphi_{B1}^0) + x_A \cdot K_{AB} \cdot \Delta h_{AB}^* \cdot \frac{\varphi_{B1} \cdot (1 - K_A \cdot \varphi_{A1})}{(V_B/V_A) \cdot (1 - K_B \cdot \varphi_{B1}) + K_{AB} \cdot \varphi_{B1}} - \frac{P_M^* \cdot V_c^E}{\tilde{V}_M} \quad (24)$$

$$H_p^E = (V_A^* \cdot x_A + V_B^* \cdot x_B) \cdot \left[ \frac{\Phi_A \cdot P_A^*}{\tilde{V}_A} + \frac{\Phi_B \cdot P_B^*}{\tilde{V}_B} - \frac{P_M^*}{\tilde{V}_M} \right] - \quad (25)$$

$$V^E = V_c^E + V_p^E \quad (26)$$

$$V_c^E = x_A \cdot K_A \cdot \Delta v_A^* \cdot (\varphi_{A1} - \varphi_{A1}^0) + x_B \cdot K_B \cdot \Delta v_B^* \cdot (\varphi_{B1} - \varphi_{B1}^0) + x_A \cdot K_{AB} \cdot \Delta v_{AB}^* \cdot \frac{\varphi_{B1} \cdot (1 - K_A \cdot \varphi_{A1})}{(V_B/V_A) \cdot (1 - K_B \cdot \varphi_{B1}) + K_{AB} \cdot \varphi_{B1}} \quad (27)$$

$$V_p^E = (V_A^* \cdot x_A + V_B^* \cdot x_B) \cdot (\tilde{V}_M - \Phi_A \cdot \tilde{V}_A - \Phi_B \cdot \tilde{V}_B) \quad (28)$$

Eqs. (17-19) and (23-28) become identical with eqs. (4-12) if  $K_B = K_{AB} = 0$  and  $K_A > 0$ . Binary alcohol/amine systems studied with this extended version of the ERAS model are listed in Table 2. In case of mixtures containing triethylamine (TEA)  $K_B$  is equal to zero assuming that TEA does not associate. Unknown parameters appearing in eqs. (17-28) are the cross parameters  $K_{AB}$ ,  $\Delta h_{AB}^*$ ,  $\Delta v_{AB}^*$ ,  $X_{AB}$  and  $Q_{AB}$ .  $K_{AB}$ ,  $\Delta h_{AB}^*$ ,  $X_{AB}$  and  $Q_{AB}$  are adjusted simultaneously to  $H^E$  and  $G^E$  using eqs. (17) and (23). Adjustment of  $X_{AB}$  is restricted to a range between 2 and 14 J/cm<sup>3</sup>.  $\Delta v_{AB}^*$  is adjusted separately to experimental data of  $V^E$ . Results of calculated excess functions and comparison with experimental data are shown in Figs. 4-6.

## DISCUSSION AND CONCLUSIONS

Comparison of calculated and experimental excess properties of binary amine/alkane and amine/alcohol systems shows that the ERAS model is able to describe all excess functions ranging from positive values in the amine/alkane systems to strong negative values found in the alcohol/amine systems. Since the molecular association mechanism involved in the extended version of the ERAS model is assumed to be close to the physical reality the parameters adjusted to the mixing properties have a certain physical meaning. Their values can be expected to reveal some interesting facts concerning the nature of different kinds of hydrogen bondings. Association constants  $K_A < 1$  are observed for amines as given in Table 1. They are smaller by more than two orders of magnitude than those found for alcohols ( $100 < K_{\text{alcohol}} < 1000$ ). Hydrogen bonding energies  $\Delta h_A^*$  of the amine self-association are only 50 per cent or even less than values found for alcohol self-association. -8.5 kJ/mol and -13.2 kJ/mol are the values for diethylamine and butylamine respectively, whereas -25.1 kJ/mol is found for alcohols. Nagata et al. (ref. 28) estimate -11 to -15 kJ/mol for  $\Delta h_A^*$  of amines. Values of  $\Delta v_A^*$ , the hydrogen bonding volume, are also smaller for amines (-2.8 and -4.7 cm<sup>3</sup>/mol) than for alcohols (see Table 1). These results indicate not only that the NH-group is a weaker proton donator than the OH-group,

they also suggest that steric hindrance may play a role in forming the hydrogen bonding in the amine self-association because more side groups are involved than in case of the OH...O bonding. The strong negative values of  $H^E$  and  $V^E$  observed experimentally for alcohol/amine systems require values for  $\Delta h_{AB}^*$  and  $\Delta v_{AB}^*$  which are much more negative than those obtained for amine and alcohol selfassociation (see Table 2).  $\Delta h_{AB}^*$ -values between -32 kJ/mol and -45 kJ/mol are obtained from the ERAS model. Particularly high  $K_{AB}$ -values are found for methanol/amine and ethanol/amine systems. Values of about -15 cm<sup>3</sup>/mol are obtained for  $\Delta v_{AB}^*$  which exceed those of alcohol and amine selfassociation by three times and more. Dutta Choudhury and Mathur (refs. 17 and 29) have obtained similar results ( $\Delta h_{AB}^* = -35$  kJ/mol) by using an estimation method which is free of a molecular model. Sawamura et al. (ref. 29) report  $\Delta v_{AB}^* = -10.7$  cm<sup>3</sup>/mol for  $\Delta v_{AB}^*$  of phenol/triethylamine measured directly by pressure dependence of UV light absorption of phenol. These authors estimate -32.6 kJ/mol for  $\Delta h_{AB}^*$ .  $X_{AB}$  values given in Table 2 are in the same range as those determined from adjusting  $X_{AB}$  to mixtures of nonpolar components such as hydrocarbons (refs. 31 and 32). It may be concluded from this result that  $X_{AB}$  represents also the difference of nonpolar intermolecular energies in associated mixtures. We assume that cross complexes in alcohol/amine mixtures have the structure OH...N. The strong interaction which exceeds the OH...O interaction considerably can be interpreted qualitatively by the fact that the free electron pair located at the N-atom has a higher polarizability and therefore acts as a more efficient proton acceptor for the -OH groups than the -OH group itself. Quantum mechanical study of hydrogen bondings in the H<sub>2</sub>O/NH<sub>3</sub> system confirm the results obtained in our work. It has been shown by Allen (ref. 33) that bonding energies of O-H...O in water is about -31 kJ/mol, the corresponding value for the N-H...N bonding in ammonia is about -16 kJ/mol. The energies for the cross bonding O-H...N and N-H...O are -36 kJ/mol and -16 kJ/mol respectively indicating the energetic superiority of the O-H...N structure compared to N-H...O.

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