BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN　VOL. 43　2671—2676 (1970)

Studies on Associated Solutions. II. Heat of Mixing of Methanol with Aliphatic Amines

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(Received November 19, 1969)

The heat of mixing has been measured at 25.00°C and 45.00°C for binary mixtures of methanol with *n*-butylamine, diethylamine and triethylamine. A twin-type conduction calorimeter was used. All the systems exhibit large negative enthalpies of mixing, which become slightly less negative as the temperature increases. From the present results and vapor-liquid equilibrium data, the excess free energy and entropy of mixing at 25.00°C have been calculated for each system. The sign and magnitude of the excess functions were as follows: $H^M < TS^E < G^E < 0$ for methanol with *n*-butylamine and diethylamine, $G^E > 0$, $TS^E < H^M < 0$ for methanol with triethylamine. These facts were interpreted in terms of steric effects and specific solvation in the hydrogen bonding between hydroxyl group and amino bases.

Since Barker's theory based on a lattice model appeared,[1] theories of associated solutions have been developed by Prigogine and Defay,[2] Kehiaian and Sonkowaska-Kehiaian[3], and Renon and Prausnitz.[4] The theories interpreted with considerable success the behavior of excess functions of some types of associated solutions, such as those composed by an associated liquid (*e.g.*, aliphatic alcohol) and a nonpolar liquid (*e.g.*, hydrocarbon, CCl_4). Although there remains much ambiguity as to the species, role and behavior of the associated complex, we can visualize these solutions as being useful as a basis for more elaborate theoretical treatment.

However, for the solutions in which both components are associated, we have at present no satisfactory theory nor important experimental information. If the modes of association in both components are similar to each other, we may expect nearly ideal behavior for their mixtures. Mixtures of two aliphatic alcohols are such examples.[5] On the other hand, the mixtures with components each having a different mode of association exhibit peculiar anomalies in their thermodynamic properties. Aqueous solutions of alcohol are typical examples of those systems which show much complexity in their structural and thermodynamic properties.[6] We can expect many other combinations of associated liquids to show similar anomalies hitherto not yet fully understood.

Apart from general interest in associated solutions, we have paid attention in particular to the thermodynamic properties of aliphatic amine+alcohol solutions. It was found that a positive deviation from the ideal solution occurs with a methanol+triethylamine (Et_3N) solution, while binary solutions of methanol with *n*-butylamine (*n*-$BuNH_2$) and diethylamine(Et_2NH) have negative excess free energies.[7] On the other hand, the infrared spectra[8] indicate that the N–OH interactions in these solutions are always stronger than those for H–OH. Thus the question arises as to why G^E is positive, in other words, which of H^M and TS^E is responsible for the unexpected behavior of tertiary amine. For an answer, it is necessary to measure the heat of mixing and combine the results with G^E data in order to obtain the excess entropy value.

In this paper, we will report the data for the heat of mixing in binary mixtures of methanol with above mentioned three aliphatic amines. Based on these data and the values in literature, we will discuss the relationship between the thermodynamic properties and steric effects in hydrogen bond.

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1) J. A. Barker, *J. Chem. Phys.*, **20**, 1526 (1952).

2) I. Prigogine and R. Defay, "Chemical Thermodynamics," Longmans Green, London (1954).

3) H. Kehiaian and K. Sonkowaska-Kehiaian, The series paper in *Bull. Acad. Polon. Sci., Ser. Sci. Chem.*, (1964).

4) H. Renon and J. M. Prausnitz, *Chem. Eng. Sci.*, **22**, 299 (1967).

5) W. D. Hill and M. van Winkle, *Ind. Eng. Chem.*, **44**, 205 (1952).

6) F. Franks and D. J. G. Ives, *Quart. Rev.* (London), **20**, 1 (1966).

7) a) J. L. Copp and T. J. V. Findlay, *Trans. Faraday Soc.*, **56**, 13 (1960). b) K. Nakanishi, H. Shirai and T. Minamiyama, *J. Chem. Eng. Data*, **12**, 591 (1967).

8) K. Nakanishi, S. Ichinose and H. Shirai, *Ind. Eng. Chem. Fundam.*, **7**, 381 (1968).

Experimental

Materials. All the samples were purified from the purest products commercially available according to the methods described in literature.[9] They were distilled twice before use under nitrogen with a 30 plate fractionating column. The purified samples showed no trace of impurity peaks on a gas chromatogram. Mercury was shaken with samples and then distilled.

Apparatus and Procedures. A twin-type conduction calorimeter based on the principle developed first by Tian and Calvet was used.[10] The apparatus, originally produced as model CM-502 by Oyodenki Kenkyusho Co., Japan, was modified for the purpose of detecting a very small amount of heat change. The calorimeter is surrounded by adiabatic materials and fixed in a submarine vessel. The submarine vessel is installed in a water thermostat, the temperature of which is kept within ±0.005°C. The temperature change due to the mixing is detected by the difference in thermal electromotive force of the thermoelement between the mixing vessel and the reference one. The electric potential is amplified by a dc-ac amplifier, the output signal of which is fed to an automatic pen recorder. With the present amplifying system we could detect the change $\pm 1\times 10^{-6}$ V. The maximum sensitivity is about 1.5×10^{-4}°C under the present conditions. The experimental procedure was similar to that described previously.[11]

Calibration of Apparatus. In order to check the accuracy of the calorimeter, the heats of mixing were measured for the benzene + carbon tetrachloride system at 25.00°C. The results are given in Fig. 1, together with those obtained by Larkin and McGlashan,[12] and fitted by the method of least squares to an equation of the type

$$H^M = x_1x_2[A + B(x_1 - x_2) + C(x_1 - x_2)^2 + D(x_1 - x_2)^3] \quad (1)$$

where H^M is the enthalpy of mixing, x is the mole fraction and A, B, C and D are constants. The values of the constants are given in Table 1. The standard and maximum deviations of the experimental points from Eq. (1) are 0.58 and −1.1 cal/mol, respectively. Table 1 and Fig. 1 indicate that there is a reasonable agreement between our results and those of Larkin and McGlashan within 3 percent for x_1=0.1—0.9.

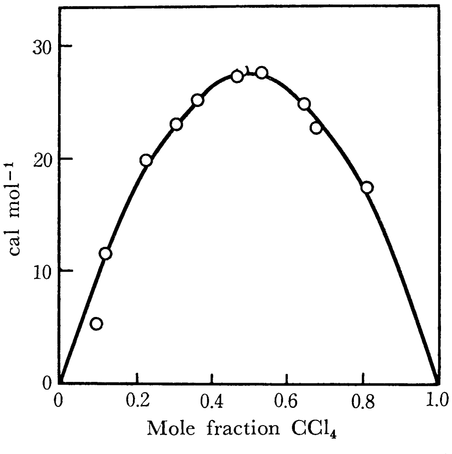

Fig. 1. Heat of mixing at 25.00°C: CCl_4+ Benzene.
—— Larkin and McGlashan
○ This Work

TABLE 1. VALUES OF CONSTANTS IN EQ. (1) FOR CARBON TETRACHLORIDE (1)+BENZENE (2) AT 25.00°C

Constants (cal/mol)	A	B	C	D
Larkin and McGlashan*	110.09	−5.58	10.27	3.35
This Work	109.79	−17.66	3.35	41.74

* Ref. 12.

Results and Discussion

Heat of Mixing. The data for the heats of mixing of binary solutions of methanol with n-$BuNH_2$, Et_2NH, and Et_3N at 25.00°C and 45.00°C are given in Tables 2 to 4 and are plotted in Fig. 2. The values of constants in Eq. (1) are given in Table 5, together with their estimated uncertainties δ, where x_1 refers to the mole fraction of methanol.

The results obtained in the present study together with a brief qualitative interpretation may be summarized as follows. 1) All the systems exhibit large negative enthalpy of mixing with the sequence of triethylamine, n-butylamine and diethylamine. The curves of H^M *vs.* x_1 (the mole

TABLE 2. HEAT OF MIXING FOR METHANOL (1) +n-BUTYLAMINE (2)

25.00°C		45.00°C	
x_1	$-H^M$ cal/mol	x_1	$-H^M$ cal/mol
0.199	453.9	0.102	229.0
0.207	483.5	0.263	618.2
0.244	569.4	0.382	769.8
0.284	605.6	0.521	884.5
0.358	773.9	0.618	843.1
0.391	801.1	0.706	768.4
0.445	857.1	0.722	742.3
0.469	878.0	0.874	425.8
0.508	886.7	0.901	311.5
0.804	602.6	0.918	280.1
0.900	305.4		

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[9] A. Weissberger and E. S. Porskauer, "Organic Solvents," Interscience Publishers Inc., New York (1955).

[10] E. Calvet and H. Prat, "Recent Progress in Microcalorimetry," Pergamon Press, London (1963).

[11] S. Murakami and R. Fujishiro, This Bulletin, **40**, 1784 (1967).

[12] J. A. Larkin and M. L. McGlashan, *J. Chem. Soc.*, **1961**, 3425.

fraction of methanol) are slightly asymmetric, each having a minimum at about $x_1=0.6$. This is consistent with the postulate that H^M results from the contributions of two effects,[13] a positive one, due to the breaking of hydrogen bonds between alcohol molecules, and large asymmetrical negative one, due to the formation of hydrogen bonds between free alcohol and amine molecules. The latter is approximately symmetrical with respect to mole fraction.

Table 3. Heat of mixing for methanol (1) +diethylamine (2)

25.00°C		45.00°C	
x_1	$-H^M$ cal/mol	x_1	$-H^M$ cal/mol
0.239	655.5	0.302	762.3
0.269	701.1	0.341	858.1
0.285	803.3	0.445	1002.1
0.362	906.3	0.624	995.3
0.401	1011.1	0.701	880.2
0.515	1091.5	0.853	523.9
0.556	1096.5	0.908	350.0
0.598	1094.5		
0.605	1091.0		
0.667	1090.6		
0.706	1029.0		
0.740	900.7		
0.846	566.2		
0.932	256.3		

Table 4. Heat of mixing for methanol (1) +triethylamine (2)

25.00°C		45.00°C	
x_1	$-H^M$ cal/mol	x_1	$-H^M$ cal/mol
0.201	219.4	0.327	300.7
0.235	238.0	0.398	344.1
0.349	312.3	0.551	455.0
0.409	386.6	0.601	460.9
0.450	424.5	0.685	453.8
0.509	455.9	0.906	240.6
0.532	487.6	0.935	223.8
0.698	440.1		
0.867	303.9		
0.903	231.2		

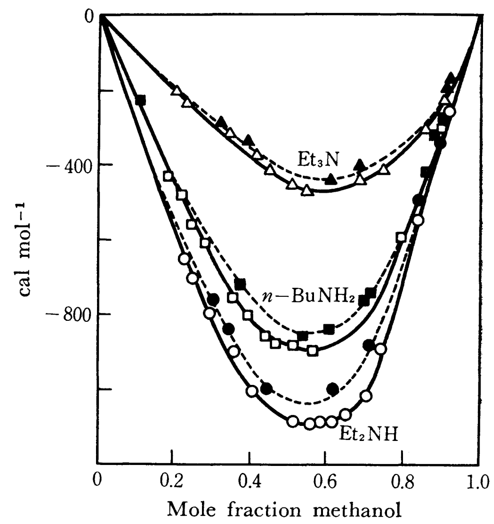

Fig. 2. Heat of mixing: MeOH + n-BuNH$_2$, Et$_2$NH, Et$_3$N.
—— 25°C, ---- 45°C

2) There is a slight tendency for H^M to become less negative as the temperature increases, that is, the excess heat capacity C_p^E is small and positive. The order of magnitude for C_p^E is less than 3 cal/deg. mole. This fact is in contrast to the system of alcohols[14] or aliphatic amines[15] with nonpolar liquids for which the temperature dependence of H^M is fairly large. This suggests that the hydrogen bonding OH–N is somewhat stronger than the OH–H hydrogen bonding in alcohols or NH–N in amines and that moderately stable complexes between alcohol and amine are formed. In fact,

Table 5. Values of constants in eq (1) for methanol (1)+aliphatic amine (2) and estimated uncertainties

Amine	Temp. (°C)	Constants (cal/mol)				δ
		A	B	C	D	
n-Butylamine	25.00	−3617.1	−1095.6	+852.9	+997.5	2.1
	45.00	−3537·9	−588.9	+677.7	−219.5	2.2
Diethylamine	25.00	−4457.1	+47.4	+2606.3	−2383.1	3.1
	45.00	−4163.2	−553.1	+1568.0	−1124.3	0.8
Triethylamine	25.00	−1776.4	−1020.4	−274.4	+230.8	2.4
	45.00	−1676.5	−678.3	+1120.4	+2900.6	4.1

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[13] J. S. Rowlinson, in "Hydrogen Bonding," paper for symposium, Ljubljana, Pergamon Press, London (1957), p. 423.

[14] J. E. A. Ottersted and R. W. Missen, *Trans. Faraday Soc.*, **58**, 879 (1962).

[15] H. Wolff and R. Wirtz, *Ber. Bunsenges. Phys. Chem.*, **72**, 101 (1968).

Lambert and Zeegers-Huyskens[16] have shown calorimetrically that there is a considerably large association energy for some aliphatic alcohols with aliphatic amines.

Other Excess Functions. The excess free energy of mixing has been calculated from isobaric vapor-liquid equilibrium data[8] by means of equations

$$\mu_1{}^E = \boldsymbol{R}T \ln (y_1P/x_1P_1) + (P_1 - P)(V_1 - B_{11}) + 2P\delta B_{12}y_2{}^2 \qquad (2)$$

$$\mu_2{}^E = \boldsymbol{R}T \ln (y_2P/x_2P_2) + (P_2 - P)(V_2 - B_{22}) + 2P\delta B_{12}y_1{}^2 \qquad (3)$$

$$G^E = x_1\mu_1{}^E + x_2\mu_2{}^E \qquad (4)$$

In the present case, the correction factors due to the vapor phase imperfection can be neglected.[8] The G^E values at 25.00°C can be evaluated from these data, since the heat of mixing has been measured as a function of temperature. For this purpose, the Gibbs-Helmholtz equation was used in the form

$$(G^E/T)_{T_2} - (G^E/T)_{T_1} = -\int_{T_1}^{T_2} H^M \mathrm{d}T/T^2 \qquad (6)$$

The excess entropies of mixing at 25.00°C have been calculated from the analytically smoothed values of H^M and G^E.[*1]

The results for each system are shown in Figs. 3—5. We see that the sign and magnitude of excess functions are as follows: $H^M < TS^E < G^E < 0$ for methanol with *n*-butylamine and diethylamine, $G^E > 0$, $TS^E < H^M < 0$ for methanol with triethylamine. For all the systems, both H^M and S^E exhibit large negative deviations, while the absolute value of G^E is relatively small owing to the counterbalance of two contributions, H^M and TS^E.

On the other hand, a large volume contraction has been observed in methanol solution with aliphatic amines. The absolute values of excess volumes of mixing were in the increasing order of *n*-BuNH$_2$, Et$_3$N and Et$_2$NH.[17] This sequence is not same as that for H^M.

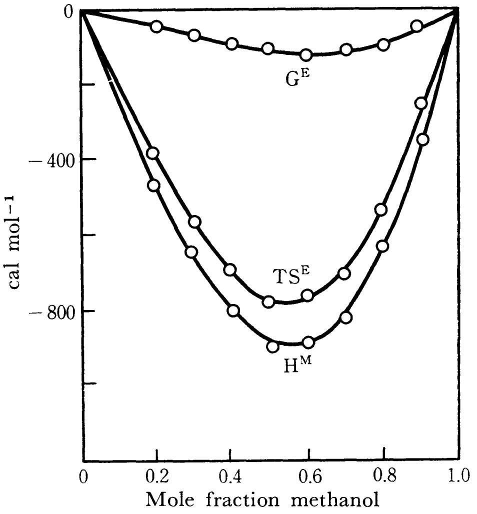

Fig. 3. Excess thermodynamic functions at 25.00°C: MeOH + *n*-BuNH$_2$.

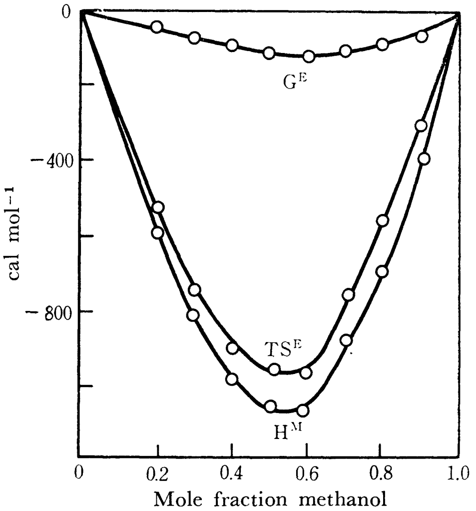

Fig. 4. Excess thermodynamic functions at 25.00°C: MeOH + Et$_2$NH.

Steric and Solvation Effects on H^M. The above results reveal that the thermodynamic properties of MeOH+Et$_3$N solution are somewhat anomalous, that is, G^E becomes positive because the absolute value of TS^E is larger than that of H^M. In the following discussions, we will compare this with other evidences for the purpose of examining the effects of geometric characteristics on physical and chemical properties.

The specific interaction between alcohol and amine, which makes the values of H^M negative, is due to a strong hydrogen bond between hydroxyl and amino groups. This interaction can be considered as the reaction between alcohol as a Lewis acid and amine as a Lewis base. An absolute Lewis base strength of aliphatic amines may be measured by the ionization potential, I, and the acidic dissociation constant, p*Ka*. Kaufman and Koski[18] estimated the ionization potential of alipha-

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[16] L. Lambert and T. Zeegers-Huyskens, *J. Chim. Phys.*, **60**, 435 (1963).

[*1] Strictly speaking, evaluation of S^E at 25.00°C should be made with the G^E values obtained at the same temperature. With lack of such data, we have used those at varying temperatures. However, for the present purpose of comparing the sign and the relative magnitude of excess functions, this may be justified since the excess heat capacity of the present system is very small as evident from Tables 2—4.

[17] K. Nakanishi and H. Shirai, This Bulletin, **43**, 1643 (1970).

[18] J. J. Kaufman and W. S. Koski, *J. Amer. Chem. Soc.*, **82**, 3262 (1960).

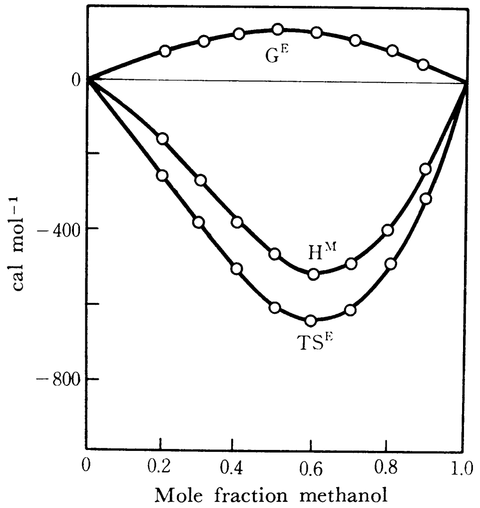
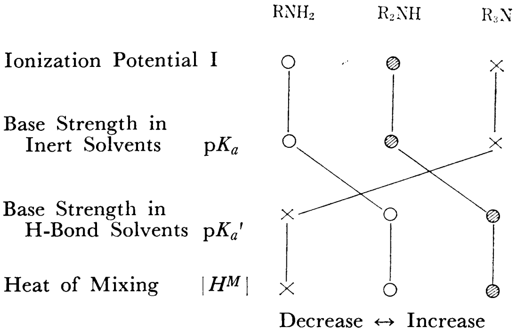


Fig. 5. Excess thermodynamic functions at 25.00°C: MeOH + Et_3N.

tic amines and defined the order as follows: $NH_3 < RNH_2 < R_2NH < R_3N$. The order is coincident with that for p*Ka* of aliphatic amines predicted by induced effect.

On the other hand, in hydrogen bonding solvents such as water or dioxane, the base strength or reactivity of amine with H^+ does not vary in the same manner.[19] We see that the order for this reactivity is in accordance with that for H^M obtained in the present work:



The phenomena, *viz.*, inversions of the sequence, have been ascribed to the steric strains and/or specific solvation effects.[20–22]

Brown *et al.*[23–25] have proposed that there should be two kinds of steric effect in determining the dissociation constant of amine. They defined them as B-strain and F-strain. The term, B-strain,[23] refers to the interference which is localized at the back of the molecule, and the term, F-strain,[24–25] refers to the repulsions due to the bulky alkyl groups in an ion pair. In the present case, rather bulky ethyl groups attached to the small nitrogen atom in Et_3N molecule tend to repel each other. This sets up the B-strain which reduces the stability of the hydrogen bonded complex, but co-ordination of an acidic proton of alcohol with the nitrogen atom of Et_3N does not cause an appreciable F-strain. Thus a certain amount of B-strain may be responsible for the relative decrease of alcohol-tertiary amine interaction, and the negative contribution to H^M will become smaller.

Another important factor which might influence H^M is the specific solvation. The amino hydrogen is considered to be a weak acidic proton, and co-ordinates to oxygen atom of alcohol. The interaction due to solvation is not as large compared with hydrogen bonding between hydroxyl group and amino bases, but it would affect the stability of hydrogen bonded complexes to some extent. Since tertiary amine has no acidic proton, its proton accepting ability is exceedingly small in comparison with that of primary or secondary amine. Thus, the two effects might be responsible for the smaller H^M of alcohol with tertiary amine system, though it is impossible to determine the dominant factor. Since no inversion in the order between R_2NH and RNH_2 is observed, steric and other effects for these two kinds of amine may be negligible.

The negative contribution discussed above is even larger than positive contributions due to the break-up of self-association of both components. In the present case, the contribution due to the break-up of alcohol structure is common to all the systems. A possible positive contribution due to the break-up of amine association should be proportional to the amino hydrogen contact number.[26] Since this contribution is negligible for Et_3N, the H^M value with Et_3N is expected to become more negative. The fact that this is not the case furnishes another support to the above interpretation.

There have been many works on the steric effects of hydrogen bonding in sterically hindered alcohols and phenols.[27–30] The low equilibrium constants of self-association have often been as-

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[19] R. G. Peason and D. C. Vogelsong, *J. Amer. Chem. Soc.*, **80**, 1038 (1958).

[20] D. H. Everett and W. F. K. Wynne-Jones, *Proc. Roy. Soc.* (London), **A177**, 499 (1941).

[21] R. G. Peason, *J. Amer. Chem. Soc.*, **70**, 204 (1948).

[22] A. F. Trotman-Dickenson, *J. Chem. Soc.*, **1949**, 1293.

[23] H. C. Brown, H. Bartholomay, Jr, and M. D. Taylor, *J. Amer. Chem. Soc.*, **66**, 435 (1944).

[24] H. C. Brown, *J. Chem. Soc.*, **1956**, 1248.

[25] H. C. Brown, *J. Amer. Chem. Soc.*, **67**, 1452 (1945).

[26] K. Sonkowska-Kehiaian, K. Orzel and H. Kehiaian, *Bull Acad. Polon. Sci., Ser. Sci. Chem.*, **14**, 711 (1966).

[27] B. G. Somers and H. S. Gutowsky, *J. Amer. Chem. Soc.*, **67**, 303 (1945).

[28] I. Yamaguchi, This Bulletin, **34**, 451 (1961).

[29] S. Singh and C. N. R. Rao, *J. Phys. Chem.*, **71**, 1074 (1967).

[30] S. Singh and C. N. R. Rao, *J. Amer. Chem. Soc.*, **88**, 2142 (1966).

cribed exclusively to entropy factors. In the present case where the alkyl groups attached to nitrogen atom are not too bulky, an enthalpy factor seems to be responsible for anomalous behavior of excess functions.

The authors thank Mr. Isao Matsumoto for his assistance in some of the experiments.