Thermochimica Acta, 88 (1985) 241–246
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

MOLAR EXCESS ENTHALPIES FOR AQUEOUS SOLUTIONS OF 2-CHLOROETHANOL AND 2-BROMOETHANOL AT 298.15 K*

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ABSTRACT

Heats of mixing for two aqueous solutions of haloalcohols, 2-chloroethanol and 2-bromoethanol, have been measured for the whole composition range at 298.15 K with an LKB 2107 flow calorimeter. The mixing is endothermic for these solution, except for highly water-rich region. The enthalpic virial coefficient has been evaluated from the data in dilute aqueous solution.

INTRODUCTION

In aqueous solutions of nonelectrolytes which have both hydrophilic and hydrophobic groups, hydrophobic hydration and hydrophobic interaction (ref.1) play an important role especially in dilute region. The hydrophobic hydration is referred to a structural promotion of water due to the introduction of nonpolar molecules or nonpolar groups of polar molecules such as alcohols, and the hydrophobic interaction to a self-association of solutes through nonpolar groups. These phenomena have been examined so far almost exclusively with thermodynamic properties, especially for aqueous alcohol solutions. In order to understand them at the molecular level, however, it is highly desirable to know the relation of thermodynamic properties to the structural and spectroscopic properties of the solution. In the case of aliphatic alcohols, the molecules consist of only C, O and H atoms and their spectroscopic features do not show much difference from those of water. However, if one deals with a group of molecules which contain heavier atoms and still exhibit an interaction with water that is similar to alcohols, one may obtain useful information easier for the present purpose. Haloalcohols may be qualified as such compounds. We have already studied the case of fluoroalcohols (ref.2). But, the introduction of F atoms leads to no favorable situation for structural and spectroscopic studies. Therefore, we have adopted in this study Cl- or Br-containing alcohols

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*Aqueous solutions of haloalcohols. II.

#JSPS post-doctoral research fellow. On leave of absence from Institute of Physical Chemistry, Polish Academy of Science, Warsaw (Poland) as solutes and measured heats of mixing with particular emphasis on dilute aqueous solution region at 298.15 K.

EXPERIMENTAL

Samples

The haloalcohols used in this study are 2-chloroethanol(ethylene chlorohydrin, denoted hereafter as MCE) and 2-bromoethanol (ethylene bromohydrin, denoted as MBE).* MCE was purified simply by repeated distillations with a column of 30 theoretical plates under reduced N_2 atmosphere, as no suitable drying agent is suggested in the literature (ref.3). The purified sample was stored in a sealed glass vessel unless used immediately. The purity of MCE used was checked by a g.l.c. analysis with a Porapak column and found to be an impurity level of less than 0.005 %. The sample of MBE was used without further purification because of its highly corrosive nature. Its impurity level was necessarily higher than that of MCE, but it was found to be less than 0.015 %. Some physical properties of the haloalcohols used are as follows.

MCE:	density/g cm^{-3}	1.1968 (this work at 298.15 K) 1.1912 (ref.4 at 303 K)
	boiling point/K	401.6 (this work) 401.8(ref.4) both at 1 atm.
MBE:	density/g cm^{-3}	1.7524 (this work) 1.7630(ref.4) both at 298.15 K
	boiling point/K	329.2 (this work) 329.7(ref.4) both at 20 mmHg

The sample of water was de-ionized, fractionally distilled and degassed three times by freezing in dry ice-methanol mixture and thawing under vacuum.

Apparatus

The heat of mixing was measured with an LKB model 2107 flow calorimeter and an LKB microperpex pump. The calibration of the calorimeter has been described elsewhere (ref.2). During the measurement, the calorimeter was kept at 298.15 ± 0.05 K and the total error in the heat of mixing value is less than 1 % for MCE or as small as 1.5 % for MBE.

As a complemental measurement, we have also attempted to establish the apparent molar volumes of haloalcohols from solution density. A Shibayama vibrating tube-type densimeter model SS-D-200 has been used for this purpose.

RESULTS AND DISCUSSION

Molar excess enthalpies for the whole composition range

The molar excess enthalpies H^E for the whole composition range of MCE + H_2O and MBE + H_2O mixtures are given in Table 1 and plotted against the mole

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*We have also attempted to use 3-chloropropanol-1. However, aqueous solution of this compound shows partial miscibility between 0.05 and 0.35 (mole fraction of the haloalcohol).

TABLE 1

Molar excess enthalpies for 2-chloroethanol + water and 2-bromoethanol + water at 298.15 K

x[a]	H^E[b]	x	H^E	x	H^E	x	H^E
			$(1 - x)\ H_2O + x\ ClCH_2CH_2OH$				
0.0489	-104.47	0.3000	326.89	0.5625	502.60	0.8008	332.42
0.1037	-28.63	0.3396	376.08	0.6067	494.04	0.8626	247.29
0.1525	68.75	0.3913	426.87	0.6585	470.20	0.9157	162.10
0.2045	170.28	0.4615	484.23	0.7102	436.32	0.9625	78.57
0.2553	272.15	0.5070	500.30	0.7484	395.81		
			$(1 - x)\ H_2O + x\ BrCH_2CH_2OH$				
0.0280	-40.48	0.2529	379.66	0.5088	637.03	0.7421	540.95
0.0544	-6.18	0.3052	453.03	0.5501	645.02	0.8132	441.83
0.1032	103.71	0.3652	525.89	0.5993	640.99	0.8806	314.80
0.1575	217.01	0.4183	573.02	0.6573	611.84	0.9231	214.48
0.2057	308.93	0.4511	595.98	0.7097	577.22	0.9735	73.10

[a] x is the mole fraction of haloalcohol.

[b] H^E is the molar excess enthalpy in J mol^{-1}.

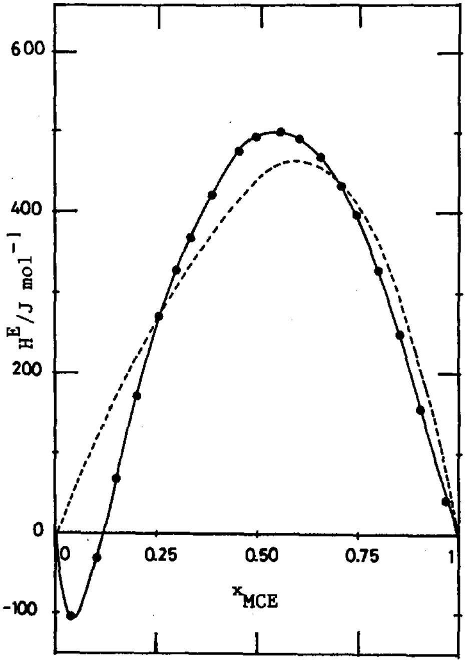

Fig. 1. Molar excess enthalpies for 2-chloroethanol + water at 298.15 K. • Experimental value, ———, ----- Calculated values(see text).

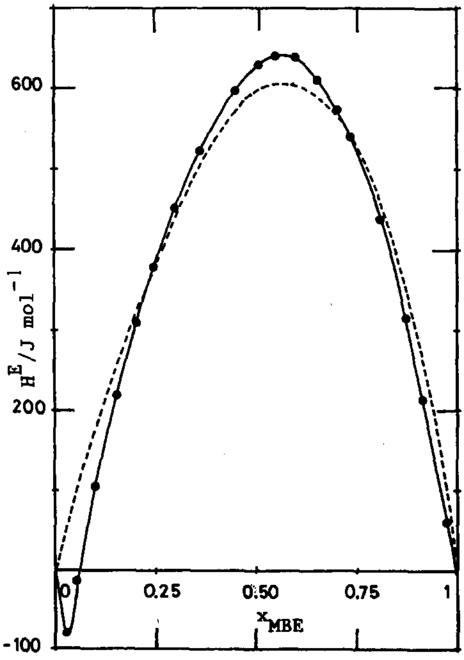

Fig. 2. Molar excess enthalpies for 2-bromoethanol + water at 298.15 K. • Experimental value, ———, ----- Calculated values(see text).

fraction of haloalcohol in Figs. 1 and 2. These two mixtures exhibit similar heat of mixing behavior; the mixing is exothermic only in water-rich region and becomes endothermic with increasing the alcohol fraction. The maximum values of H^E are about 500 J mol^{-1} for MCE solutions and 650 J mol^{-1} for MBE solutions, respectively, at $x \cong 0.55$.

While this kind of S-shape H^E vs. x data is very difficult to correlate by empirical equation, their qualitative interpretation seems to be fairly simple because similar H^E behavior has already been observed for aqueous alcohol solutions. First we will discuss the correlation problem. For this purpose are available two types of empirical equation, namely, conventional Redlich-Kister expansion and the local composition model. We found that the number of terms (parameters) required for reasonable reproduction of the present data is as large as 8. Obviously, no clear physical meaning can be given for such parameters. If we use only 3 or 4 parameters as usual, the result is discouraging as shown by dotted curves in Figs. 1 and 2. The NRTL equation in the local composition model gives quite similar results. However, the present data can be satisfactorily correlated by a modified NRTL equation proposed by one of us (ref.5). This new equation contains an additional term which describes the self-association of haloalcohols and its temperature dependence. As shown by the solid curves in Figs. 1 and 2, calculated H^E values agree almost perfectly with the experimental data. The root mean square deviation is as large as 5.7 J mol^{-1} for the both solutions.

An extensive study has been made by Larkin (ref.6) for the measurement of H^E in ethanol + water mixtures as a function of temperature. According to their results, the mixing is exothermic in the whole composition range at room temperature but tends to endothermic in ethanol-rich region gradually with increasing temperature. This is the same tendency as that when the alcohol becomes higher. The present results thus indicate that the introduction of halogen atoms into ethanol is equivalent to the increase in the size of hydrophobic group in alcohol. Furthermore, it is a common feature that H^E increases almost linearly with the mole fraction of alcohol after taking a minimum value. This means that the partial molar enthalpy of alcohols is nearly constant in a certain composition range (pseudo two-phase system (ref.6)).

Molar excess enthalpies in water-rich region

The enthalpic virial coefficient h_{xx} can be obtained from accurate H^E data in highly dilute aqueous solution. An additional H^E measurements have been made for this purpose. The results are shown in Table 2 and plotted in Figs. 3 and 4. It is found that the minimum values of exothermic H^E are approximately -110 J mol^{-1} at $x \cong 0.05$ for MCE solution and -55 J mol^{-1} at $x \cong 0.035$ for MBE solution, respectively. From a linear relation between H^E and the molarity of halo-

TABLE 2

Molar excess enthalpies for water-rich region of 2-chloroethanol + water and 2-bromoethanol + water at 298.15 K

x^a	$H^{E\,b}$	x	H^E	x	H^E	x	H^E
$(1 - x)\ H_2O + x\ ClCH_2CH_2OH$							
0.0027	-10.9	0.0199	-71.2	0.0493	-111.3	0.1024	-29.7
0.0052	-20.8	0.0243	-92.2	0.0585	-103.4	0.1180	6.7
0.0075	-30.5	0.0310	-94.4	0.0700	-92.9	0.1307	32.7
0.0096	-38.3	0.0372	-103.8	0.0700	-100.8	0.1494	67.8
0.0116	-45.0	0.0430	-109.9	0.0816	-70.6	0.1672	103.3
0.0147	-55.0	0.0478	-125.2	0.0880	-55.9		
$(1 - x)\ H_2O + x\ BrCH_2CH_2OH$							
0.0024	-7.7	0.0126	-33.3	0.0304	-54.0	0.0602	-13.0
0.0035	-10.7	0.0154	-43.9	0.0349	-54.7	0.0674	8.5
0.0044	-13.6	0.0157	-41.6	0.0410	-52.4	0.0726	14.3
0.0058	-21.1	0.0192	-45.3	0.0449	-47.8	0.0859	50.8
0.0067	-19.9	0.0218	-48.5	0.0496	-42.0	0.0945	77.6
0.0091	-25.5	0.0254	-51.7	0.0555	-22.5	0.1051	101.3
0.0116	-34.5						

[a] x is the mole fraction of haloalcohol.

[b] H^E is the molar excess enthalpy in J mol^{-1}.

alcohol, both h_{xx} and the partial molar enthalpy of haloalcohol at infinite dilution $\bar{H}^E$ have been evaluated as in the following.

	MCE	MBE
$\bar{H}^E$/kJ mol^{-1}	-4.14	-3.30
h_{xx}/J kg mol^{-2}	260	950

These results indicate that the hydrophobic hydration is larger for MCE but the hydrophobic interaction is larger for MBE.

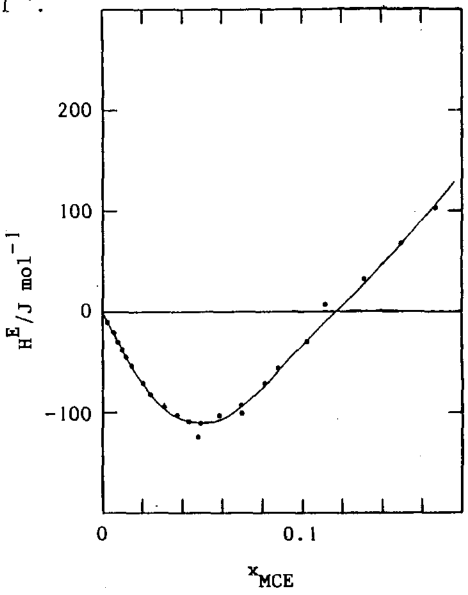

Fig. 3. Molar excess enthalpies for water-rich region of 2-chloroethanol + water mixture at 298.15 K

Apparent molar volumes of haloalcohols

The apparent molar volume ϕ of haloalcohols evaluated from density data exhibits a characteristic behavior that is common to aliphatic alcohols

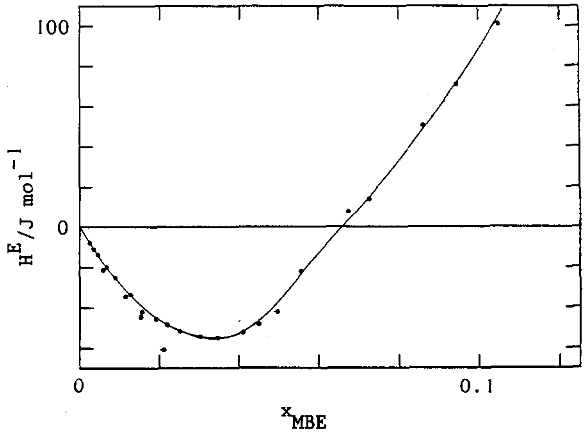

Fig. 4. Molar excess enthalpies for water-rich region of 2-bromoethanol + water mixture at 298.15 K

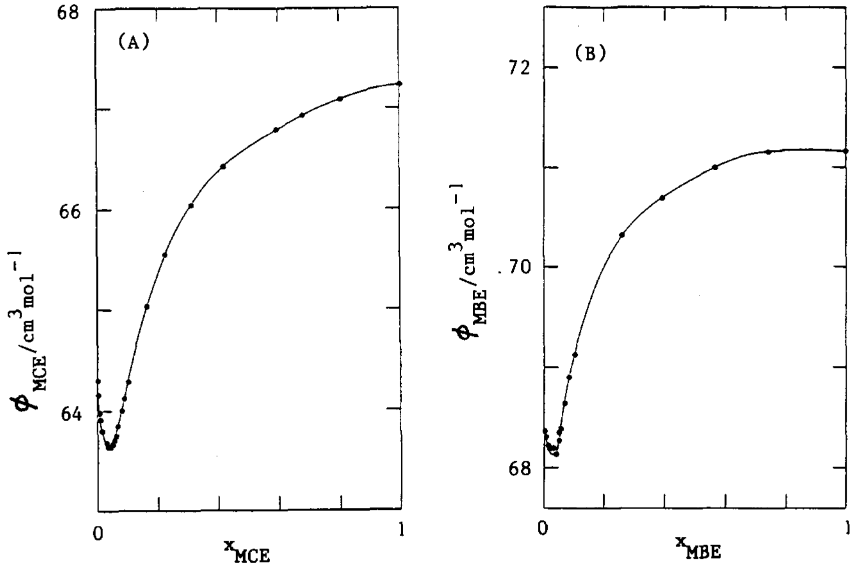

Fig. 5. Apparent molar volumes of haloalcohols in water at 298.15 K. (A): 2-chloroethanol. (B): 2-bromoethanol.

as in Fig. 5. The results of light scattering study will be reported later.

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