

**INTERPRETATION OF HEATS OF MIXING
OF 1-BUTANOL, 2-BUTANOL AND 2-METHYL-2-PROPANOL
WITH CYCLOHEXANE IN TERMS OF SOME MODELS
OF CONTINUOUSLY ASSOCIATED SOLUTION***

František VESELÝ, Vladimír DOHNAL, Miriam VALENTOVÁ and Jiří PICK

Department of Physical Chemistry,

Prague Institute of Chemical Technology, 166 28 Prague 6

Received January 19th, 1983

Three models of continuously associated solution complemented by an assumption of polynomial temperature dependence of corresponding interaction parameters were used for simultaneous description of the concentration and temperature dependence of heats of mixing of 1-butanol, 2-butanol and 2-methyl-2-propanol with cyclohexane. Very good results were reached for the first two systems where the Liebermann and Wilhelm model has proved to be the most suitable. With respect to the probable existence of cyclic associates in solutions of 2-methyl-2-propanol, none of the used models which assume only linear association satisfied to the extent required.

In a foregoing paper¹ we have published experimental data on heats of mixing of cyclohexane with 1-butanol, 2-butanol, 2-methyl-2-propanol in the entire range of mole fraction of the respective alcohol and for six isotherms within 25 to 50°C.

The aim of this work is a quantitative interpretation of the concentration and temperature dependence of enthalpies of mixing of these systems in terms of models of continuously associated solution designated in the literature as the Renon and Prausnitz model² (RP) modified by Hildebrand, Prausnitz and Scott³ (HPS) and in a variant by Liebermann and Wilhelm⁴ (LW).

THEORETICAL

The assumptions of Kretschmer and Wiebe⁵, on which all the three models were derived, have formerly been discussed⁶ in detail, and therefore we present here only the final relations with the same meaning of symbols as in works cited^{2,4,6}.

The total heat of mixing H^E is usually divided into two parts

$$H^E = H_c^E + H_p^E . \quad (1)$$

* Part XXIX in the series Enthalpy Data of Liquids; Part XXVIII: This Journal 48, 3482 (1983).

The contribution H_c^E is denoted as the chemical part of heat of mixing given by the formation of associates of a polar component. For the RP, HPS and LW models it holds that

$$H_c^E = K \Delta H^0 x_B (\phi_{B1} - \phi_{B1}^*), \quad (2)$$

where

$$\phi_{B1} = \frac{4\phi_B}{[1 + \sqrt{(1 + 4K\phi_B)}]^2}, \quad \phi_{B1}^* = \lim_{x_B \rightarrow 1} \phi_{B1},$$

$\phi_B(x_B)$ is the volume (mole) fraction of alcohol, K and ΔH^0 are the equilibrium association constant and standard enthalpy of association.

The physical part H_p^E in Eq. (1) follows from interactions of nonspecific (physical) character, and is expressed differently in each model.

In the RP model the equation of the van Laar type⁷

$$H_p^E = \beta' \phi_A \phi_B (x_A V_A + x_B V_B) \quad (3)$$

has been used, where β' is the interaction parameter and V_A , V_B are molar volumes of hydrocarbon and alcohol, respectively.

The HPS model stems from the regular solution concept³

$$H_p^E = (x_A S_A + x_B S_B) \xi_A \xi_B h_{AB}, \quad (4)$$

where

$$\xi_A = x_A S_A / (x_A S_A + x_B S_B), \quad \xi_B = 1 - \xi_A.$$

The quantities S_A , S_B characterize the size of molecule and were interpreted as a measure of molecule surface

$$S_A/S_B = (V_A/V_B)^{2/3}.$$

The adjustable parameter h_{AB} has the meaning of exchange energy related to a surface unit.

The LW model expresses the physical interactions by the Bruin equation⁸ which leads to the relation with one adjustable constant A :

$$H_p^E = \frac{ACG_P^E \ln A}{1 - \ln A} \left(\frac{x_B}{x_A + x_B A} + \frac{x_A}{x_B + x_A A} - \frac{1}{A \ln A} \right), \quad (5)$$

where

$$G_p^E = \frac{-2RTx_Ax_B \ln A}{(x_A + x_B A)(x_B + x_A A)}$$

and

$$C = 2 - \frac{2AK \Delta H^0}{RT \ln A} \left(\frac{V_A/V_B}{\sqrt{(1+4K)[1+\sqrt{(1+4K)}]^2}} \right).$$

Similarly to cyclohexane with propanols⁶, also here we have complemented all the models by the assumption that the temperature dependence of the parameters β' , h_{AB} and A may be expressed by the empirical relation

$$X = a + bT + cT^2. \quad (6)$$

Since according to the starting assumptions⁵ all alcohols have the same standard enthalpy of association, and the association constant of alcohol does not depend on the nature of inert solvent, it is sufficient to determine the constant K in Eq. (2) at one temperature and the parameters a , b , c in Eq. (6) for the simultaneous description of the concentration and temperature dependence of H^E .

Our task was to decide which of the above-mentioned models is most suited for the mixtures studied, and to what extent it is possible to assume the existence of linear associates only even for 2-methyl-2-propanol.

RESULTS AND DISCUSSION

When calculating heats of mixing on the basis of the models mentioned we proceeded in the following way:

The molar volumes of pure components were considered as temperature independent⁶ in the interval 25–50°C, and the given values (in cm³/mol) were taken over from the literature⁹: $V_A = 110.29$, $V_B = 93.01$ (1-butanol); 93.47 (2-butanol); 96.89 (2-methyl-2-propanol).

The standard enthalpy of association had for all the alcohols the value⁶ of -25.1 kJ mol⁻¹.

For each system we calculated the parameters A from Eqs (1), (2) and (5) by an iteration procedure for a set of assumed K values for single experimental $H^E(x_B, T)$ data. (Just as well we could determine K by means of the HPS and RP models. We used the LW model only for this reason that the computer program was available from our former work⁶.) The sum of deviations of parameters A from an average value was determined. Minimum of this sum corresponded to the optimum value of K .

In this way we found $K(50^\circ\text{C}) = 80$ for 1-butanol, which is in absolute agree-

ment with the value which is reported by Nagata¹⁰. Similarly we determined for the remaining two alcohols (association constants of this type have not been published yet) that K (50°C) = 70 (2-butanol) and 110 (2-methyl-2-propanol).

By using the above-mentioned procedure, we obtained simultaneously the constants A in the LW model for each system and single temperatures, and evaluated

TABLE I

Heats of mixing of 1-butanol, 2-butanol and 2-methyl-2-propanol with cyclohexane; comparison of standard deviations σ (J mol⁻¹) and mean absolute deviations δ (%) for the RP, HPS and LW models

$t, ^\circ\text{C}$	m^a	σ			δ		
		RP	HPS	LW	RP	HPS	LW
1-butanol							
25	26	12.89	12.01	11.26	2.85	2.67	2.26
30	25	13.90	13.74	12.32	2.95	2.73	2.37
35	25	19.78	18.22	15.31	3.88	3.57	2.94
40	23	25.66	23.94	20.51	4.71	4.37	3.74
45	27	32.59	30.58	26.51	5.30	4.92	4.23
50	25	40.98	38.85	34.68	5.38	5.06	4.48
	151	25.96	24.39	21.42	4.18	3.89	3.34
2-butanol							
25	23	19.94	17.55	16.96	3.01	2.66	2.48
30	23	20.88	18.25	16.87	2.78	2.41	2.20
35	24	23.74	20.96	18.45	2.80	2.34	1.98
40	26	26.03	23.05	19.09	2.62	2.15	1.79
45	28	29.68	26.40	20.69	2.66	2.18	1.63
50	25	35.56	32.32	25.60	2.85	2.35	1.85
	149	26.30	23.46	19.58	2.78	2.34	1.97
2-methyl-2-propanol							
30	24	48.19	51.02	55.19	7.04	7.43	7.72
35	24	45.36	47.55	49.23	5.49	5.75	5.87
40	26	42.72	44.06	45.61	5.05	5.27	5.58
45	24	51.83	51.92	51.53	4.94	5.10	5.30
50	25	48.49	47.16	46.79	3.71	3.84	4.12
	123	46.57	47.55	48.87	5.23	5.46	5.72

^a Number of measurements.

the parameters a , b , c in Eq. (6) from them:

1-butanol

$$A = 0.1043 - 6.744 \cdot 10^{-3}T + 14.1 \cdot 10^{-6}T^2, \quad (7)$$

2-butanol

$$A = 1.8791 - 5.488 \cdot 10^{-3}T + 6.1 \cdot 10^{-6}T^2, \quad (8)$$

2-methyl-2-propanol

$$A = -2.4200 + 21.73 \cdot 10^{-3}T - 36.8 \cdot 10^{-6}T^2. \quad (9)$$

The parameters β' and h_{AB} were evaluated for the same K as in the LW model by the method of least squares from Eqs (1), (2) and (3) or (4), respectively. Their temperature dependences in the form of Eq. (6) are given in the original work¹¹.

The comparison of experimental excess enthalpies with the values of heats of mixing calculated in terms of the RP, HPS and LW models is carried out in Table I in the form of standard deviations σ and mean absolute percent deviations δ .

All the models give satisfactory results for the systems 1-butanol+cyclohexane and 2-butanol+cyclohexane. For both the systems the lowest deviations are found at all the temperatures in case of the LW model. Therefore we have limited ourselves only to this model when comparing the terms H_c^E and H_p^E in Eq. (1) and when calculating H^E of 1-butanol and 2-butanol with other nonpolar solvents (see below).

If we in the end judge the results at the same time from the point of view of the concentration and temperature dependence, the LW model represents 151 experi-

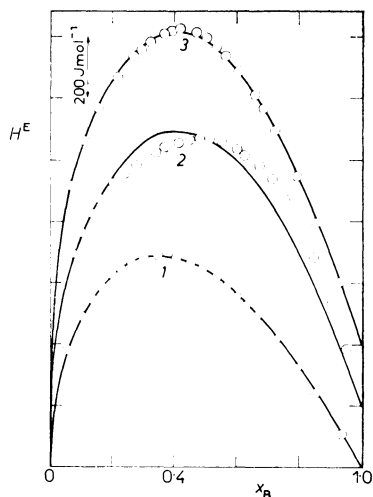


FIG. 1
Dependence of heats of mixing H^E (J mol^{-1}) of 1-butanol 1, 2-butanol 3 and 2-methyl-2-propanol 2 with cyclohexane at 30°C on mole fraction of alcohol x_B ; points: experimental values, curves: calculated from the LW model

TABLE II
Comparison of contributions H_c^E and H_p^E ($J mol^{-1}$) for $x_B = 0.4$

$t, ^\circ C$	H^E	H_c^E	H_p^E	$H_p^E/H^E, \%$
1-butanol				
25	626.1	457.0	169.1	27.0
30	683.5	492.3	191.2	28.0
35	745.4	528.7	216.7	29.1
40	810.9	566.1	244.8	30.2
45	881.4	604.3	277.1	31.4
50	956.3	643.3	313.0	32.7
2-butanol				
25	944.8	483.2	461.6	48.9
30	1 012.0	520.3	491.7	48.6
35	1 080.9	558.4	522.5	48.3
40	1 151.7	597.5	554.2	48.1
45	1 223.6	637.3	586.3	47.9
50	1 297.3	678.0	619.3	47.7

TABLE III
Calculation of heats of mixing from the LW model for alkanes with 1-butanol and 2-butanol^a

System	$t, ^\circ C$	m	A	$\delta, \%$	Ref.
n-Butane + 1-butanol	25	33	0.9299	6.14	16
n-Pentane + 1-butanol	25	17	0.9048	5.86	17
n-Hexane + 1-butanol	25	14	0.8810	3.38	18
	25	8	0.8883	2.39	19
	35	9	0.8635	1.96	
	45	8	0.8363	2.86	
n-Hexane + 2-butanol	25	6	0.7897	2.25	20
	45	10	0.7535	3.74	21
Methylcyclohexane + + 1-butanol	25	21	0.8848	4.26	22
n-Decane + 1-butanol	25	48	0.8298	5.20	23

^a m is number of measurements, A parameter of Eq. (5), δ mean absolute deviation

mental values of heats of mixing in the system 1-butanol+cyclohexane by means of one constant of Eq. (2) and three constants of Eq. (7) with a standard deviation of 21.42 J/mol and mean absolute deviation of 3.34%, and for the system cyclohexane+2-butanol with the same number of constants in Eqs (2) and (8), 149 H^E data with a deviation of 19.58 J/mol and 1.97%, respectively.

It is also evident from Fig. 1 that the LW model brings out not only the position of maximum but also the course of the concentration dependence of H^E for both the systems. However, for the 2-methyl-2-propanol+cyclohexane system, not a single of models presented satisfies. The association constant appears to be unrealistically high, the calculated H^E curves do not render the position of maximum (Fig. 1), the deviations are more than double compared to the foregoing systems. This all gives evidence that the assumption of existence of the linear alcohol associates only is not fulfilled.

From a qualitative analysis of behaviour of 2-methyl-2-propanol in different solvents which was carried out by Otin, Gracia and Gutierrez-Losa^{12,13} it is evident that its association leads to the formation of non-negligible ratio of cyclic associates. Recently, French and Stokes¹⁴ have suggested the model of associated solution which stems from the assumption of simultaneous existence of linear and cyclic associates of polar component in diluted solutions of nonpolar solvents. Extension of the model to the whole concentration region of alcohol¹⁵ raises hopes for considerable advance in theory of associated solutions. This problem will be dealt with in more detail in a next paper.

When comparing both terms on the right-hand side of Eq. (1), we have shown⁶ for the mixtures of propanols with cyclohexane that higher values of H^E for 2-propanol are explainable by a heightened ratio of nonspecific interactions which changes only little with temperature. As it can be seen from Table II, the ratio of nonspecific interactions of 1-butanol and 2-butanol has similar character. The contribution H_p^E is for these systems still about 10% higher than for C_3 -alkanols, which is in quantitative agreement with the decrease in the association constant and expressive increase in the number of physical interactions and corresponding endothermic effect.

In conclusion, the comparison is given in Table III of enthalpies of mixing of systems published in the literature, where one of components is 1-butanol or 2-butanol and the second one an alkane, with the values calculated from the LW model. The data used were not sorted and smoothed in any way. The parameter A was calculated as an average value from the interval $x_B \in \langle 0.1; 0.9 \rangle$. The calculated deviations are relatively favourable and in agreement with the results of this work.

REFERENCES

1. Veselý F., Dohnal V., Valentová M., Pick J.: This Journal 48, 3482 (1983).
2. Renon H., Prausnitz J. M.: Chem. Eng. Sci. 22, 299, 891 (1967).
3. Hildebrand J. H., Prausnitz J. M., Scott R. L.: *Regular and Related Solutions*, Reinhold Publ. Corp., New York 1970.

4. Liebermann E., Wilhelm E.: *Monatsh. Chem.* 106, 389 (1975).
5. Kretschmer C. B., Wiebe R.: *J. Chem. Phys.* 22, 1697 (1954).
6. Veselý F., Uchytíl P., Záborský M., Pick J.: *This Journal* 44, 2869 (1979).
7. Scatchard G.: *Chem. Rev.* 44, 7 (1949).
8. Bruin S.: *Ind. Eng. Chem., Fundam.* 9, 305 (1970).
9. Timmermans J.: *Physico-Chemical Constants of Pure Organic Compounds*. Elsevier, Amsterdam 1950.
10. Nagata I.: *Z. Phys. Chem. (Leipzig)* 252, 305 (1973).
11. Valentová M.: *Thesis*. Prague Institute of Chemical Technology, Prague 1982.
12. Otín S., Gracia M., Gutierrez-Losa C.: *J. Chim. Phys. Physicochim. Biol.* 70, 1227 (1973).
13. Otín S., Gracia M., Gutierrez-Losa C.: *J. Chim. Phys. Physicochim. Biol.* 71, 637 (1974).
14. French H. T., Stokes R. H.: *J. Phys. Chem.* 85, 3347 (1981).
15. Nagata I.: Private communication.
16. McFall T. A., Post M. E., Collins S. G., Christensen J. J., Izatt R. M.: *J. Chem. Thermodyn.* 13, 41 (1981).
17. Collins S. G., Christensen J. J., Izatt R. M., Hanks R. W.: *J. Chem. Thermodyn.* 12, 609 (1980).
18. Murakami S., Fujishiro R.: *Bull. Chem. Soc. Jap.* 39, 720 (1966).
19. Brown I., Fock W., Smith F.: *Aust. J. Chem.* 17, 1106 (1964).
20. Murakami S., Amaya K., Fujishiro R.: *Bull. Chem. Soc. Jap.* 37, 1176 (1964).
21. Brown I., Fock W., Smith F.: *J. Chem. Thermodyn.* 1, 273 (1969).
22. Veselý F., Mikulič A. V., Svoboda V., Pick J.: *This Journal* 40, 2551 (1975).
23. Christensen J. J., Izatt R. M., Stitt B. D., Hanks R. W.: *J. Chem. Thermodyn.* 11, 261 (1979).

Translated by J. Linek.