THERMODYNAMIC PROPERTIES OF ALCOHOL SOLUTIONS

II. ETHANOL AND ISOPROPANOL SYSTEMS

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Summary

New experimental data are given for the heats of mixing of the systems ethanol+toluene at 35 °C, ethanol+methyl*cyclo*hexane at 35 °C, and *iso*propanol+benzene at 45 °C and for the liquid-vapour equilibrium data for the latter system at 45 °C.

These data have been used together with previously published data to calculate the excess free energy, heat and excess entropy of mixing at even mole fractions for the above systems. These functions have also been calculated from published data for the systems ethanol+benzene at 45 °C and ethanol+2,2,4-trimethylpentane at 25 °C.

I. Introduction

The present work forms part of a programme of measurement of the thermodynamic properties of alcohol solutions. Data for the system ethanol+carbon tetrachloride have been given in Part I of this series by Barker, Brown, and Smith (1953) and by Brown and Fock (1955).

II. Apparatus and Methods

Heats of mixing for the systems ethanol+benzene and ethanol+2,2,4-trimethylpentane were measured previously by Brown and Fock (1955). For the other systems the methods of Brown and Fock (1956) were used.

Table 1

isopropanol+benzene

Refractive index; composition data

x_1	$n_D^{25\cdot00}$	x_1	$n_D^{25\cdot00}$
0·0528	1·49150	0·4980	1·43899
0·1067	1·48511	0·5017	1·43853
0·2087	1·47317	0·5983	1·42681
0·3057	1·46182	0·7131	1·41256
0·3931	1·45149	0·8053	1·40083
0·4898	1·43997	0·9033	1·38805
0·4932	1·43952	0·9494	1·38189

The liquid-vapour equilibrium measurements for the system *iso*propanol+benzene were made by using the apparatus and methods of Brown and Smith (1955). The analysis was by refractive index measurements with a Hilger-Chance precision refractometer maintained at 25·00±0·01 °C. The refractive index and composition data for this system are given in Table 1;

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they were obtained from mixtures prepared by weighing. The method of Brown and Smith (1954) was employed to calculate the composition of the liquid and vapour samples.

III. Components

The ethanol, benzene, and 2,2,4-trimethylpentane were purified by the methods described by Brown and Smith (loc. cit.) and Brown and Fock (loc. cit.). The *iso*propanol (Analar quality) was purified by distillation and was dried by azeotropic distillation with purified benzene in a 1·2 m column packed with 1·6 mm Dixon packing, operated at a reflux ratio of 50 : 1. The toluene was distilled using the same column and the centre fraction was scrubbed with concentrated sulphuric acid, washed, dried, and refractionated. The methyl*cyclo*hexane was purified in the same way as the toluene.

The density and refractive index values for the purified components are shown in Table 2.

Table 2

PHYSICAL PROPERTIES OF COMPONENTS

Component	$d_4^{25\cdot00}$	$n_D^{25\cdot00}$
Ethanol	0·78511	1·35928
*iso*Propanol	0·78089	1·37503
Benzene	0·87370	1·49799
Toluene	0·86224	1·49406
Methyl*cyclo*hexane	0·76515	—
2,2,4-Trimethylpentane ..	0·68778	1·38905

The vapour pressure of *iso*propanol was measured by using the equilibrium still. The vapour pressure data are shown in Table 3. These data were fitted by the method of Willingham *et al.* (1945) to the Antoine equation

$$\log P = A - \frac{B}{C+t},$$

where P is in standard mm Hg and t in °C. The values of the constants, the standard deviation σ of the fit, the calculated values of the boiling point at 760 mm Hg, and the vapour pressure at 45 °C are also given in Table 3.

Table 3

VAPOUR PRESSURE OF ISOPROPANOL

t (°C)	P (mm Hg)	Antoine Equation Constants
41·31	111·51	
44·99	135·87	$A = 7\cdot76677$
45·18	137·44	$B = 1371\cdot59$
49·09	168·41	$C = 198\cdot490$
57·72	259·00	$\sigma = 0\cdot12$ mm Hg
64·93	363·11	
70·35	462·34	B.p./760 mm Hg (°C), 82·23
75·10	566·93	V.p. 45·00 °C (mm Hg), 136·05
78·48	652·61	
82·17	758·13	
82·26	760·51	

IV. EXPERIMENTAL RESULTS

(*a*) *Heats of Mixing*

The results of the heat of mixing measurements for the systems ethanol+toluene at 35 °C, ethanol+methyl*cyclo*hexane at 35 °C, and *iso*propanol+benzene at 45 °C are given in Tables 4, 5, and 6 respectively; x_1 is the mole fraction of the alcohol and H^M is the heat of mixing in joules per mole (J/mol) of mixture

TABLE 4

HEATS OF MIXING

Ethanol+toluene 35·00 °C

x_1	H^M (J/mol)	x_1	H^M (J/mol)
0·122	859	0·676	631
0·217	983	0·681	612
0·379	998	0·691	586
0·603	738	0·873	264
0·605	740		

TABLE 5

HEATS OF MIXING

Ethanol+methyl*cyclo*hexane 35·00 °C

x_1	H^M (J/mol)	x_1	H^M (J/mol)
0·129	574	0·712	478
0·247	685	0·719	515
0·426	695	0·719	506
0·657	553	0·723	470
0·665	529	0·888	276
0·670	541	0·892	257

TABLE 6

HEATS OF MIXING

*iso*Propanol+benzene 45·00 °C

x_1	H^M (J/mol)	x_1	H^M (J/mol)
0·118	1163	0·495	1687
0·131	1213	0·499	1638
0·233	1552	0·571	1548
0·284	1637	0·581	1521
0·490	1655	0·816	866

(b) *Liquid-Vapour Equilibrium Data*

The liquid-vapour equilibrium data for the system *iso*propanol + benzene at 45 °C are given in Table 7 ; x_1 and y_1 are the mole fractions of *iso*propanol in the liquid and vapour respectively, P is the total pressure in standard mm Hg and α is the relative volatility.

Graphs of the data in Table 7 show that *iso*propanol + benzene forms an azeotrope at 45·00 °C, having a mole fraction of 0·296 *iso*propanol at a total pressure of 273·4 mm Hg.

Table 7

EXPERIMENTAL DATA AND DERIVED FUNCTIONS

*iso*Propanol + benzene at 45·00 °C

x_1	y_1	P	α	μ_1^E	μ_2^E	G_x^E
0·0472	0·1467	252·50	3·470	1108·3	6·0	58·0
0·0980	0·2066	264·13	2·397	889·8	22·8	107·8
0·2047	0·2663	272·06	1·410	601·6	71·8	180·3
0·2960	0·2953	273·40	0·9966	436·3	126·7	218·3
0·3862	0·3211	272·22	0·7517	317·8	187·4	237·8
0·4753	0·3463	269·49	0·5848	227·8	256·6	242·9
0·5504	0·3692	264·92	0·4781	164·5	321·2	235·0
0·6198	0·3951	259·35	0·4007	118·8	387·8	221·1
0·7096	0·4378	247·70	0·3187	69·0	483·5	189·4
0·8073	0·5107	227·14	0·2491	30·3	601·8	140·4
0·9120	0·6658	189·28	0·1922	6·8	744·1	71·7
0·9655	0·8252	159·80	0·1687	0·8	821·8	29·1

V. Excess Free-Energy Data

The values of the excess chemical potentials μ_1^E, μ_2^E and the excess free energy of mixing G_x^E for the system *iso*propanol + benzene were calculated from the data given in Table 7, using equations (**1**), (**2**), and (**3**) :

$$\mu_1^E = RT \ln Py_1/P_1x_1 + (\beta_{11} - V_1)(P - P_1) + P\delta_{12}y_2^2 + \tfrac{1}{3}D_{11}\{(4y_1^3 - 3y_1^4)P^3 - P_1^3\}, \qquad \ldots\ldots \quad (1)$$

$$\mu_2^E = RT \ln Py_2/P_2x_2 + (\beta_{22} - V_2)(P - P_2) + P\delta_{12}y_1^2 - D_{11}\{y_1^4P^3\}, \qquad \ldots\ldots \quad (2)$$

$$G_x^E = x_1\mu_1^E + x_2\mu_2^E, \qquad \ldots\ldots\ldots\ldots\ldots\ldots \quad (3)$$

where P_1 and P_2 are the vapour pressures of the pure components, V_1 and V_2 the liquid molar volumes, β_{11}, β_{22}, β_{12}, and D_{11} are coefficients in the equations of state for the pure and mixed vapours. δ_{12} is given by

$$\delta_{12} = 2\beta_{12} - \beta_{11} - \beta_{22}.$$

The equation of state for the pure component vapours was taken as

$$V = RT/P + \beta_{jj} + D_{jj}P^2,$$

and that for the mixed vapour as

$$V_{12}=RT/P+\beta_{11}y_1^2+2\beta_{12}y_1y_2+\beta_{22}y_2^2+D_{11}y_1^4P^2.$$

The value of D_{22} for benzene was assumed to be zero and the values of the other coefficients were calculated from equations given by Kretschmer and Wiebe (1954) for *iso*propanol and by Allen, Everett, and Penney (1952) for benzene. The value of β_{12} was evaluated by the method given by Brown and Smith (1954).

The values of the coefficients at 45 °C were :

β_{11}	β_{22}	β_{12}	δ_{12}	V_1	V_2	D_{11}	D_{22}
—2·15	—1·23	—0·97	1·44	0·079	0·092	$-1\cdot195\times10^{-5}$	0

Units are l/mol except D_{11}, which is in l/mm² mole.

The values of the correction terms involving D_{11} in equations (1) and (2) were less than 1 cal/mol.

Values of the derived thermodynamic functions are given in Table 7 in calories per mole of mixture.

The excess free-energy data were fitted by the method of least squares to equation (4)

$$G_x^E=x_1x_2[a+b(x_1-x_2)+c(x_1-x_2)^2]. \quad \dots\dots\dots\dots \quad (4)$$

The values of the constants in this equation and the standard deviation σ of the fit were found to be, in cal/mol,

$$a=963\cdot7,\quad b=-173\cdot0,\quad c=134\cdot3,\quad \sigma=1\cdot7.$$

These values do not indicate separation into two liquid phases.

The excess free-energy data were shown to be thermodynamically consistent by comparing the areas above and below datum on a plot of $\mu_1^E-\mu_2^E$ against x_1 ; their ratio was 1·002.

The excess free energy of mixing for the systems containing 2,2,4-trimethylpentane, toluene, and methyl*cyclo*hexane was calculated from the experimental data of Kretschmer, Nowakovska, and Wiebe (1948) and Kretschmer and Wiebe (1949*a*, 1949*b*). The non-ideality of the vapours was allowed for by using the method of Brown and Smith (1954), values of β_{22} being calculated from the Berthelot equation. The values used were (l/mol)

2,2,4-Trimethylpentane 25 °C ..	—2·34
Toluene 35 °C	—1·75
Methyl*cyclo*hexane 35 °C	—1·90

The excess free-energy data for the system ethanol+benzene have been determined by Brown and Smith (1954).

VI. THERMODYNAMIC PROPERTIES

The excess free energy G_x^E, heat of mixing H_x^M, and excess entropy of mixing TS_x^E for the five alcohol systems were calculated at even mole fractions, at the temperature of measurement, from the data given in the earlier sections of the

Table 8

THERMODYNAMIC PROPERTIES

Ethanol + benzene 45 °C

x_1	G^E_x	H^M_x	TS^E_x
0·1	125	230	+105
0·2	202	294	+92
0·3	247	315	+68
0·4	267	312	+45
0·5	268	285	+17
0·6	250	241	— 9
0·7	215	189	—26
0·8	160	132	—28
0·9	88	68	—20

Table 9

THERMODYNAMIC PROPERTIES

Ethanol + toluene 35 °C

x_1	G^E_x	H^M_x	TS^E_x
0·1	140	182	+42
0·2	213	231	+18
0·3	258	243	—15
0·4	286	235	—51
0·5	288	210	—78
0·6	267	178	—89
0·7	231	140	—91
0·8	172	97	—75
0·9	98	50	—48

Table 10

THERMODYNAMIC PROPERTIES

Ethanol + 2,2,4-trimethylpentane 25 °C

x_1	G^E_x	H^M_x	TS^E_x
0·1	158	123	— 35
0·2	250	150	—100
0·3	304	162	—142
0·4	334	161	—173
0·5	340	152	—188
0·6	321	138	—183
0·7	284	119	—165
0·8	225	93	—132
0·9	136	57	— 79

present paper. T °K$=t$ °C$+273\cdot16$, 1 cal$=4\cdot1840$ abs. joules. These data are given in cal/mol of mixture in Tables 8 to 12. For the systems containing toluene, methyl*cyclo*hexane, and 2,2,4-trimethylpentane Kretschmer, Nowakowska, and Wiebe (1948) and Kretschmer and Wiebe (1949*a*, 1949*b*) calculated heats of mixing from the excess free-energy data at two temperatures. Their values are approximately 30 per cent. higher and more symmetrical in mole fraction than the directly measured values given above.

TABLE 11

THERMODYNAMIC PROPERTIES

Ethanol+methyl*cyclo*hexane 35 °C

x_1	G^E_x	H^M_x	TS^E_x
0·1	165	121	— 44
0·2	254	158	— 96
0·3	306	168	—138
0·4	334	167	—167
0·5	339	159	—180
0·6	320	143	—177
0·7	280	122	—158
0·8	217	94	—123
0·9	126	59	— 67

TABLE 12

THERMODYNAMIC PROPERTIES

*iso*Propanol+benzene 45 °C

x_1	G^E_x	H^M_x	TS^E_x
0·1	110	251	141
0·2	177	350	173
0·3	219	397	178
0·4	240	408	168
0·5	241	393	152
0·6	225	357	132
0·7	193	299	106
0·8	145	222	77
0·9	80	123	43

VII. DISCUSSION

The results given here, together with the results of Scatchard and Ticknor (1952) for methanol+benzene and those of Barker, Brown, and Smith (1953) for ethanol+carbon tetrachloride, enable some interesting comparisons to be made.

If we compare the thermodynamic properties of the ethanol systems we find that those having non-aromatic components are similar, while those with aromatic components have more positive values of the excess entropy and heat of mixing. This indicates stronger interaction of alcohol molecules with aromatic than with non-aromatic molecules. This causes increased breaking of alcohol hydrogen bonds and this occurs at a higher concentration of alcohol in aromatic systems than in non-aromatic systems.

Comparison of the systems containing benzene with different alcohols shows that the heat and excess entropy of mixing become rapidly more positive as the hydrocarbon chain of the alcohol molecule becomes longer. More positive heats of mixing could be due either to a larger heat change on breaking an individual hydrogen bond or to the fact that more hydrogen bonds are broken in solutions of longer-chain alcohols. Increased heat of breaking individual hydrogen bonds would be expected to lead to more *negative* excess entropy of mixing. The second alternative, however, is consistent with the observed increase of both heat of mixing and excess entropy of mixing with alcohol chain-length. If more hydrogen bonds are broken at a given concentration in systems with longer-chain alcohols, this can only be because the entropy increase on breaking an individual hydrogen bond is larger in these systems. This is presumably associated with a larger gain in configurational freedom on breaking hydrogen bonds between longer-chain alcohol molecules. It is uncertain how far this increase continues as the size of the alcohol molecule increases, but the corresponding properties calculated from less reliable data listed in Appendix I for *n*-propanol+benzene and the four butanol+benzene systems suggest that the properties of the butanol systems are not very different from those of the *iso*propanol system.

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IX. References

Allen, P. W., Everett, D. H., and Penney, M. F. (1952).—*Proc. Roy. Soc.* A **212** : 149.
Allen, B. B., Lingo, S. P., and Felsing, W. A. (1939).—*J. Phys. Chem.* **43** : 425.
Barker, J. A., Brown, I., and Smith, F. (1953).—*Disc. Faraday Soc.* **15** : 142.
Brown, I., and Fock, W. (1955).—*Aust. J. Chem.* **8** : 361.
Brown, I., and Fock, W. (1956).—*Aust. J. Chem.* **9** : 180.
Brown, I., and Smith, F. (1954).—*Aust. J. Chem.* **7** : 264.
Brown, I., and Smith, F. (1955).—*Aust. J. Chem.* **8** : 501.
Kretschmer, C. B., Nowakowska, J., and Wiebe, R. (1948).—*J. Amer. Chem. Soc.* **70** : 1785.
Kretschmer, C. B., and Wiebe, R. (1949*a*).—*J. Amer. Chem. Soc.* **71** : 1793.
Kretschmer, C. B., and Wiebe, R. (1949*b*).—*J. Amer. Chem. Soc.* **71** : 3176.
Kretschmer, C. B., and Wiebe, R. (1954).—*J. Amer. Chem. Soc.* **76** : 2579.
Lee, S. C. (1931).—*J. Phys. Chem.* **35** : 3558.
Olsen, A. L., and Washburn, E. R. (1937).—*J. Phys. Chem.* **41** : 457.
Pahlke, H. (1935).—" Landolt-Börnstein Tabellen." (Springer : Berlin.)
Perrakis, N. (1925).—*J. Chim. Phys.* **22** : 296.
Scatchard, G., and Ticknor, L. B. (1952).—*J. Amer. Chem. Soc.* **74** : 3724.
Willingham, C. B., Taylor, W. J., Pignocco, J. M., and Rossini, F. D. (1945).—*J. Res. Nat. Bur. Stand.* **35** : 219.

APPENDIX I

n-Propanol + benzene 40 °C	(Lee 1931)
*iso*Propanol + benzene 25 °C	(Olsen and Washburn 1937)
n-Butanol + benzene 25 °C	(Allen, Lingo, and Felsing 1939)
*iso*Butanol + benzene 25 °C	
sec.-Butanol + benzene 25 °C	
tert.-Butanol + benzene 25 °C	
n-Propanol + benzene 20 °C	(Pahlke 1935)
*iso*Propanol + benzene 20 °C	
tert.-Butanol + benzene 20 °C	
n-Butanol + benzene 20 °C	(Perrakis 1925; Pahlke 1935).