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Studies on Associated Solutions. I. Excess Volume of Binary Systems of Alcohols with Various Organic Liquids

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Excess volumes of mixing have been determined at 25.00°C by pycnometry for eleven binary solutions of methanol and two binary solutions of ethanol with organic liquids. The second components include three aliphatic amines, *n*-butyraldehyde, ethyl acetate, isopropyl ether, anisol, chlorobenzene, acetonitrile, pyridine and nitromethane. The excess volumes of binary solutions containing aliphatic alcohols, which are evaluated from the available density data, were critically reviewed and compared with the present results.

The specific interaction due to the hydrogen bond between the polar groups of different components is primarily responsible for the non-ideal behaviors of binary associated solutions. In binary solutions containing alcohols, for example, the hydrogen bond energy between the hydroxyl group in the alcohol

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molecules and the proton acceptor group in the other component is estimated to be more than 2 kcal/mol, while the interactions between the inert groups such as the aliphatic hydrocarbon portion of the molecules are almost negligible. This is why the simple lattice theory as proposed by Barker[1] proved considerably successful in interpreting the behavior of the excess functions of associated solutions such as benzene + methanol or chloroform + acetone.

When an alcohol is mixed with other organic compounds, part of alcohol molecules will tend to dissociate from the polymeric aggregates through the hydrogen bond to form other kinds of hydrogen bonds with different kinds of molecules. The degree of dissociation from polymeric species would be dependent on the proton accepting ability of the functional group in the molecule. As a rough first approximation, this may be the most decisive factor in determining the sign and magnitude of the deviation from the ideal solution law.[2]

It is the purpose of the present studies to investigate in detail the dependence of each thermodynamic property of the mixtures of polar and associated liquids including alcohols on the nature of component liquids. The present paper deals with the volume of mixing for thirteen binary solutions containing methanol or ethanol as one component. The results are discussed with available data.

Experimental

Purification of Liquids. Samples of alcohols and other organic liquids were the same as in our recent vapor-liquid equilibrium studies.[3,4] They were prepared as follows. Available reagents of the best grade were dried, whenever necessary, over dehydrating agents such as CaO, and then distilled with a 30 plates fractionating column under atmospheric or reduced nitrogen pressure. Only the middle fraction was used. When the liquids are highly hygroscopic, they are re-distilled immediately before use.

Density Measurement. The densities of pure liquids and solutions were determined with a bicapillary-type pycnometer.[5-7] The capacity of the pycnometer was 10 m*l*. All the measurements were carried out at 25.00°C in a thermostat. The temperature was controlled to ±0.005°C. The present density data seems to be accurate within ±0.00005 g/m*l*.

Results and Discussion

Density and Excess Volume Data. The density data d_{12} were converted to the excess volumes of mixing V^E by means of

$$V^E = \frac{x_1M_1 + x_2M_2}{d_{12}} - \left(x_1\frac{M_1}{d_1{}^0} + x_2\frac{M_2}{d_2{}^0}\right) \tag{1}$$

where x is mole fraction, M is molecular weight, d^0 is density of pure liquid, and subscript 1 refers to alcohols. V^E values for each solution were then fitted to the equation

$$V^E = x_1(1-x_1)\sum_{n=0}^{2}A_n(1-2x_1)^n \tag{2}$$

where constants A_n were determined by the method of least squares.[*1]

The density and excess volume data are presented in Table 1 and the latter is plotted in Fig. 1. The constants in Eq. (2) and the excess volume for equimolar mixture, $(V^E)_{x_1=x_2}$, are listed in Table 2. As is evident from Eq. (2), the values $(A_0+A_1+A_2)$ and $(A_0-A_1+A_2)$ represent the terminal values of V^E/x_1x_2 at $x_1=0.0$ and $x_1=1.0$. Thus, they are equivalent to $\bar{v}_i-v_i{}^0$, the difference between the molar volume of pure liquid and the partial molar volume of the same liquid at infinite dilution. They are also shown in Table 2.

The excess volumes of all the systems investigated are negative for the whole composition ranges. The only exception is the nitromethane-rich region of ethanol+nitromethane systems. As seen in Table 2, the largest volume contraction in methanol solutions is observed with *n*-butyraldehyde, which is followed by aliphatic amines (Et_2NH, Et_3N, and *n*-$BuNH_2$), isopropyl ether, pyridine in this order. Other polar liquids show smaller volume contraction. The volume contraction in ethanol solutions is smaller than that in corresponding methanol solutions. It should be remarked that constant A_1 is always negative, which means $\bar{v}_1-v_1{}^0$ is more positive than $\bar{v}_2-v_2{}^0$.

Literature Survey. In order to interpret the present data, we found it necessary to compare them with available data. Therefore, we have made an extensive literature survey and analyzed the density data of binary solutions containing methanol, ethanol, propanols, or butanols as a component. The results are summarized in Table A (see Appendix) by listing the value of $(V^E)_{x_1=x_2}$ $(=0.25\ A_0)$ for each system. Most of the data published be-

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

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

3) K. Nakanishi, H. Shirai and K. Nakasato, *J. Chem. Eng. Data*, **13**, 188 (1968).

4) K. Nakanishi, R. Toba and H. Shirai, *J. Chem. Eng. Japan*, **2**, 4 (1969).

5) K. Nakanishi, This Bulletin, **33**, 793 (1960).

6) K. Nakanishi, N. Kato and M. Maruyama, *J. Phys. Chem.*, **71**, 814 (1967).

7) K. Nakanishi, H. Touhara, K. Sato and M. Nagao, This Bulletin, **41**, 2536 (1968).

[*1] As seen in Table 1 and Fig. 1, the precision with which the V^E values are established is sometimes not enough for evaluating three constants in Eq. (2). This is the case especially for the systems having small absolute values of V^E. However, it is revealed that the V^E/x_1x_2 *vs.* x_1 plot, though not shown here, cannot be approximated by a straight line. Thus, it is necessary to assign three constants for each system as in Table 1.

TABLE 1. DENSITIES AND EXCESS VOLUMES OF BINARY SOLUTIONS AT 25.00°C

Mole fraction of alcohols x_1	Density d_{12} (g/ml)	Excess volume V^E (ml/mol)
MeOH (1) + n-Butyraldehyde (2)		
0.0000	0.80025	0.0
0.2007	0.82740	−2.770
0.3232	0.84534	−4.174
0.4763	0.86369	−5.207
0.5759	0.86627	−5.081
0.6259	0.86393	−4.779
0.6875	0.85793	−4.234
0.7248	0.85309	−3.851
0.7691	0.84531	−3.299
0.8416	0.83057	−2.352
0.9012	0.81609	−1.516
1.0000	0.78624	0.0
MeOH (1) + Ethyl acetate (2)		
0.0000	0.89407	0.0
0.1719	0.88604	−0.050
0.3219	0.87713	−0.069
0.4856	0.86468	−0.072
0.5810	0.85574	−0.074
0.6871	0.84378	−0.072
0.7433	0.83633	−0.068
0.7871	0.82975	−0.056
0.8362	0.82184	−0.058
0.9175	0.80605	−0.031
0.9686	0.79431	−0.012
MeOH (1) + Isopropyl ether (2)		
0.0000	0.71838	0.0
0.1546	0.72511	−0.585
0.2011	0.72719	−0.711
0.3295	0.73316	−0.950
0.5117	0.74237	−1.012
0.6782	0.75302	−0.886
0.7347	0.75760	−0.822
0.7783	0.76128	−0.737
0.8200	0.76570	−0.686
0.8543	0.76866	−0.559
0.8962	0.77383	−0.472
0.9443	0.77975	−0.303
MeOH (1) + Anisol (2)		
0.0000	0.98938	0.0
0.1770	0.97532	−0.099
0.2279	0.97050	−0.118
0.3950	0.95192	−0.194
0.6643	0.90637	−0.218
0.8632	0.84977	−0.161
MeOH (1) + Chlorobenzene (2)		
0.0000	1.10103	0.0
0.1239	1.08507	−0.073
0.4908	1.01618	−0.180
0.5908	0.98895	−0.194
0.6551	0.96859	−0.205
0.7514	0.93219	−0.192
0.8559	0.88235	−0.149
0.9183	0.84541	−0.094
0.9605	0.81654	−0.046
MeOH (1) + n-Butylamine (2)		
0.0000	0.73514	0.0
0.1876	0.74477	−0.619
0.3679	0.75723	−1.260
0.4694	0.76426	−1.461
0.5472	0.76924	−1.504
0.7049	0.77818	−1.326
0.8295	0.78310	−0.903
0.9084	0.78532	−0.539
0.9487	0.78606	−0.322
MeOH (1) + Diethylamine (2)		
0.0000	0.69893	0.0
0.0775	0.70593	−0.598
0.1202	0.70970	−0.869
0.1736	0.71467	−1.196
0.2366	0.72072	−1.539
0.2682	0.72380	−1.688
0.3381	0.73071	−1.965
0.4144	0.73867	−2.209
0.4950	0.74625	−2.270
0.5953	0.75574	−2.204
0.6652	0.76186	−2.026
0.7128	0.76575	−1.845
0.7534	0.76903	−1.665
0.8046	0.77268	−1.376
0.8519	0.77596	−1.079
0.9272	0.78137	−0.568
0.9402	0.78238	−0.478
MeOH (1) + Triethylamine (2)		
0.0000	0.72284	0.0
0.0567	0.72608	−0.398
0.1288	0.73028	−0.840
0.1873	0.73383	−1.158
0.2514	0.73770	−1.435
0.2991	0.74094	−1.650
0.3438	0.74400	−1.815
0.4196	0.74939	−2.035
0.4989	0.75538	−2.189
0.5543	0.75965	−2.230
0.5996	0.76337	−2.241
0.6454	0.76658	−2.154
0.6942	0.77035	−2.052
0.7520	0.77491	−1.880
0.8525	0.78135	−1.323
0.9506	0.78561	−0.515
MeOH (1) + Acetonitrile (2)		
0.0000	0.77700	0.0
0.0786	0.77800	−0.027
0.0819	0.77801	−0.026
0.1095	0.77843	−0.039
0.2007	0.77952	−0.062

Table 1 (Continued)

Mole fraction of alcohols x_1	Density d_{12} (g/ml)	Excess volume V^E (ml/mol)
0.3391	0.78147	−0.109
0.5060	0.78386	−0.156
0.5124	0.78377	−0.146
0.5472	0.78417	−0.149
0.6176	0.78513	−0.161
0.6779	0.78586	−0.165
0.7488	0.78627	−0.142
0.8735	0.78703	−0.103
0.8970	0.78712	−0.093
0.9146	0.78714	−0.082
MeOH (1)+Pyridine (2)		
0.0000	0.97810	0.0
0.0407	0.97488	−0.065
0.1874	0.96085	−0.207
0.2638	0.95286	−0.301
0.3736	0.93954	−0.403
0.4491	0.92910	−0.462
0.5012	0.92138	−0.510
0.5497	0.91270	−0.491
0.6109	0.90163	−0.514
0.7608	0.86771	−0.445
0.8276	0.84890	−0.362
0.8919	0.82842	−0.266
0.9491	0.80727	−0.130
MeOH (1)+Nitromethane (2)		
0.0000	1.13117	0.0
0.1427	1.09411	−0.067
0.4616	0.99930	−0.170
0.5797	0.95920	−0.185
0.7157	0.90909	−0.183
0.7941	0.87805	−0.169
0.8704	0.84596	−0.133
EtOH (1)+Diethylamine (2)		
0.0000	0.69893	0.0
0.0419	0.70243	−0.239
0.1206	0.71067	−0.806
0.1734	0.71583	−1.083
0.2309	0.72119	−1.307
0.3121	0.72888	−1.566
0.4199	0.73998	−1.883
0.4808	0.74591	−1.956
0.5638	0.75351	−1.933
0.6485	0.76157	−1.861
0.7240	0.76767	−1.631
0.8098	0.77335	−1.200
0.9131	0.78062	−0.648
1.0000	0.78507	0.0
EtOH (1)+Nitromethane (2)		
0.0000	1.13090	0.0
0.1000	1.09261	0.052
0.1961	1.05727	0.060
0.3436	1.00457	0.051
0.4043	0.98333	0.043
0.4393	0.97138	0.026
0.4734	0.95973	0.015
0.5033	0.94953	0.006
0.6077	0.91429	−0.023
0.7005	0.88359	−0.058
0.7567	0.86497	−0.064
0.8039	0.84989	−0.098
0.8386	0.83838	−0.089
0.9039	0.81709	−0.086

fore 1956 have been collected by Timmermans.[8] We have used his data and also the more recent ones as shown in the footnote of the table.

Dependence of V^E on Various Factors. We call attention to the following evidence obtained from the present work and literature survey.

1. As Fig. 2 illustrates, $(V^E)_{x_1=x_2}$ increases generally with the molar volume of primary normal alcohol. For c-C_6H_{12}, Et_2O, $CHCl_3$, and Et_3N, the dependence is somewhat irregular. Since the molar volume of the second component chosen is generally larger than 80 ml/mol, the results indicate that the empirical congruent principle proposed by Brönsted[9] cannot be applied to alcohol solutions.
2. As was shown by Brown,[10] the $(V^E)_{x_1=x_2}$ values for secondary and tertiary alcohols are larger than those for the corresponding normal alcohol. This can also be verified from the cases with acetone and n-heptane.
3. The $(V^E)_{x_1=x_2}$ value increases generally with tepmerature. There are some exceptional cases. An inverse dependence is observed with phenol, aniline, and formamide. Note that they are all associated liquids.
4. As regards to the symmetricity of the excess function, it appears that highly a symmetric V^E *vs.* x relation is observed for definite type of second component (*e. g.*, $CHCl_3$, CCl_4, toluene, *etc.*). As was discussed by Rowlinson[11] and van Ness,[12] these liquids have very weak interactions with hydroxyl group and break the alcohol hydrogen bond only insufficiently. However, such high asymmetry

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[8] J. Timmermans, "Physico-Chemical Constants of Binary Systems in Concentrated Solutions, "Interscience, New York (1959).

[9] J. N. Brönsted and J. K. Koeford, *danske vidensk Selsk* (*Mat. fys. Medd*), No. 17, 22 (1946).

[10] I. Brown and F. Smith, *Aust. J. Chem.*, **15**, 1 (1962).

[11] J. S. Rowlison, "Liquids and Liquids Mixtures," 2nd Ed. Butterworths, London (1969).

[12] F. Pardo and H. C. van Ness, *J. Chem. Eng. Data*, **10**, 163 (1965).

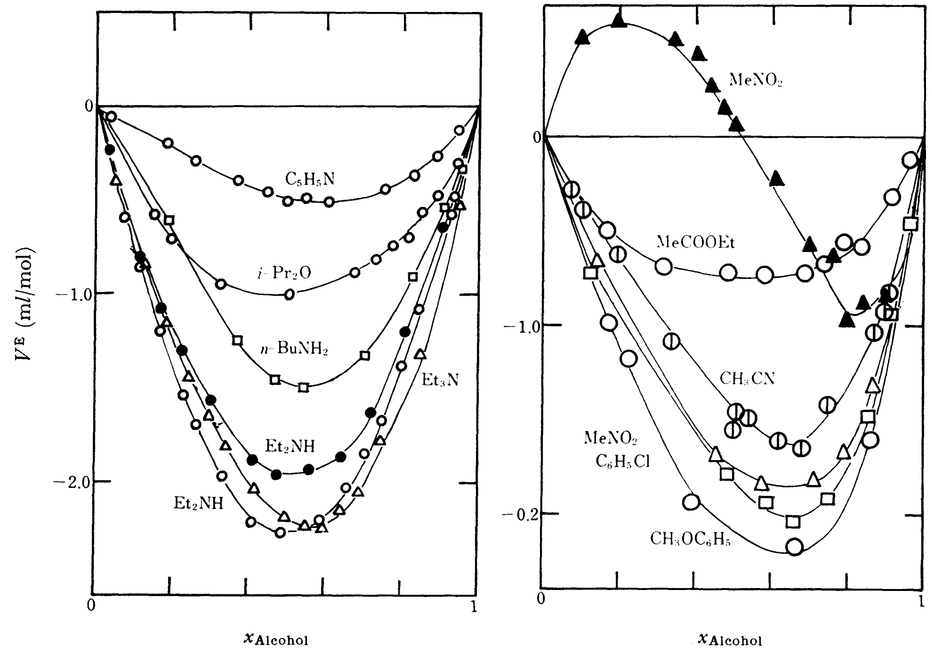

Fig. 1. Excess volumes of 13 binary solutions containing methanol or ethanol at 25°C. Filled marks indicate the data for ethanol solutions.

TABLE 2. CONSTANTS FOR EXCESS VOLUME EQUATION AND DERIVED QUANTITIES

Second component	Constants of Eq. (2)			Excess volume for equimolar mixture	Partial molar volume at infinite dilution	
	A_0	A_1	A_2	$(V^E)_{x_1=x_2}$ [a]	$\bar{v}_1-v_1^0$ [a]	$\bar{v}_2-v_2^0$ [a]
MeOH solutions						
n-Butyraldehyde	−20.553	−1.007	+7.387	−5.138	−12.159	−14.173
Ethyl acetate	− 0.305	−0.021	−0.122	−0.076	− 0.406	− 0.448
Isopropyl ether	− 3.851	−0.092	−1.816	−0.963	− 5.576	− 5.759
Anisol	− 0.840	−0.452	−0.325	−0.210	− 0.713	− 1.618
Chlorobenzene	− 0.766	−0.332	−0.256	−0.192	− 0.690	− 1.355
n-Butylamine	− 5.909	−1.912	+1.449	−1.477	− 2.549	− 6.373
Diethylamine	− 9.063	−3.281	+1.218	−2.266	− 7.517	− 8.173
Triethylamine	− 8.773	−2.094	−0.491	−2.183	− 7.130	−11.317
Acetonitrile	− 0.579	−0.389	−0.167	−0.145	− 0.357	− 1.135
Pyridine	− 1.931	−0.876	−0.176	−0.483	− 1.231	− 2.981
Nitromethane	− 0.691	−0.410	−0.310	−0.173	− 0.590	− 1.411
EtOH solutions						
Diethylamine	− 7.736	−0.585	+0.154	−1.934	− 6.997	− 8.167
Nitromethane	+ 0.044	−0.771	−0.450	+0.011	+ 0.366	− 1.176

[a] ml/mol

is not limited to the cases of practically nonpolar liquids. As an example, EtOH+dioxan or EtOH+nitromethane shows a similar trend. In the cases where the excess volume changes sign, there is always a volume contraction in alcohol-rich region.

5. There exists a sequence in the values of excess volumes of binaries with a given alcohol. The excess volume has an exceptionally large negative value of −2 to 5 ml/mol for the combination of alcohols with the liquids in which a chemical reaction might take place. Binary systems with aldehydes or acids are typical examples. Another group of binary systems which exhibit a large negative V^E is the mixture, aliphatic amine and alcohol. The V^E values are between −0.5 and −2.5 ml/mol. On the other hand, the V^E

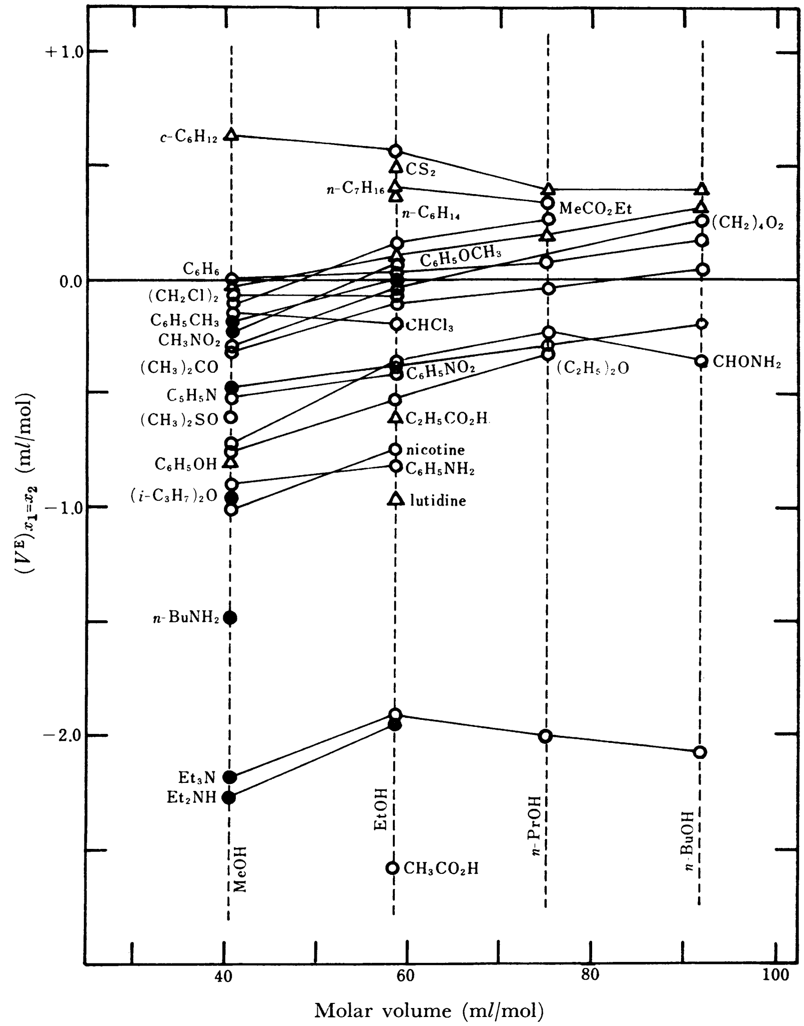

Fig. 2. Relation between excess volume at equimolar mixture and molar volume of alcohol. ● this work, ○ literature value, △ indicates the values at other temperatures than 25°C

values for the systems with paraffin hydrocarbons such as c-C_6H_{12}, n-C_6H_{14}, *etc.* are positive and usually larger than +0.3 ml/mol. The V^E values for aromatic hydrocarbons and weakly polar liquids are nearly equal to zero or slightly negative. Thus, an obvious relationship between the V^E and the proton affinity of the functional group in the second component is now widely confirmed. This sequence is also parallel with that observed in spectroscopic studies.[2,13] The variation in the values of V^E for aliphatic amines deserves attention. We will compare them with the heat of mixing data in a succeeding paper.[14]

Part of the above observations has been discussed by Brown *et al.*,[10,15] Paraskevopoulos and Missen[16] and Copp and Findlay.[17] The systems alcohol +nonpolar liquid were discussed extensively by Brown *et al.* in their recent paper.[15] We were able to reveal the V^E behaviors for a wide variety of binary solutions. Figure 1 of Ref, 15 shows the behaviors with higher alcohols in certain cases.

Qualitative Interpretation. In view of the present status of solution theories, our analysis is limited to a qualitative description, since the speci-

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[13] W. Gordy and S. C. Stanford, *J. Chem. Phys.*, **8**, 170 (1940).

[14] K. Nakanishi, H. Touhara and N. Watanabe, submitted to This Bulletin, in press.

[15] I. Brown, W. Fock and F. Smith, *J. Chem. Thermodynamics*, **1**, 273 (1969).

[16] G. C. Paraskevopoulos and R. W. Missen, *Trans. Faraday Soc.*, **58**, 869 (1962).

[17] J. L. Copp and T. J. V. Findlay, *ibid.*, **56**, 13 (1960).

fic interactions in alcohol solutions are too complicated. Paraskevopoulos and Missen[16] have concluded in their analysis of V^E data for alcohol+CCl_4 solutions that there are two contributions to the total volume change on mixing, *viz*, the break-up of the alcohol structures and the geometrical fitting of the second component into the remaining alcohol structure. Since the alcohol structure has open cavities, the first contribution should be positive. On the other hand, the geometrical fitting leads to a negative contribution, as it is a process of co-operative accommodation of the second component into the alcohol structure which is accompanied by an interstitial dissolution. This interpretation seems to be valid also for various types of binary alcohol solutions. The fact that the V^E values are generally negative indicates that the second contribution is more important in determining the sign of V^E values. For the co-operative accommodation of the second component to be effective, the molecules should have higher proton accepting ability. The second contribution may then be roughly proportional to the proton accepting ability, though the geometrical characteristics of each molecule will produce an additional effect. A comparison of the V^E data with the spectroscopic data such as "hydrogen bond shift" indicates that this is the case for binary methanol solutions. Existence of a positive contribution reflects on the positive temperature coefficient of V^E. Relative easiness of the break-up of alcohol structure may be responsible for less negative value of secondary and tertiary alcohols than primary alcohols. This will be verified by a comparison with V^E data for alcohol-alcohol mixtures, which are positive with a combination of primary and secondary alcohols. The available data are as follows; The $(V^E)_{x_1=x_2}$ value is +0.005 for MeOH+EtOH (15°C), +0.045 for MeOH+*n*-PrOH (15°C), +0.07 for MeOH+*n*-BuOH (25°C), +0.09 for MeOH+*i*-BuOH (15°C), +0.01 for EtOH+*n*-BuOH (25°C), +0.045 for EtOH+*i*-BuOH (15°C) and 0.00 for *n*-PrOH+*n*-BuOH (15°C).[8,18]

In conclusion, the present data comprise a new and important addition to our knowlegde of excess volume behavior of binary methanol solutions, for which there are less data than for ethanol.

The authors thank K. Nakasato, S. Ichinose, R. Toba and T. Minamiyama for their assistance in experimental work. They also wish to thank Professor N. Watanabe and Mr. H. Touhara for their interest and discussions.

Appendix

The density data are available in literature. We summarize the present information on V^E for binary solutions containing five lower aliphatic alcohols in Table A by listing $(V^E)_{x_1=x_2}$ value.

TABLE A. LITERATURE VALUES OF EXCESS VOLUME FOR EQUIMOLAR MIXTURE OF BINARY SOLUTIONS CONTAINING SOME ALIPHATIC ALCOHOLS

Second component	Excess volume for equimolar mixture $(V^E)_{x_1=x_2}$ (m*l*/mol)					Reference
	MeOH	EtOH	*n*-PrOH	*i*-PrOH	*n*-BuOH	
n-Hexane		+0.41(25)* +0.41(30) +0.33(6)	+0.18(25)	+0.48(22)	+0.08(25)	a, b
n-Heptane		+0.58(50) +0.42(30) +0.32(10)	+0.85(30) +0.31(25)	+0.58(25)		a, c, d
i-Octane		+0.59(50) +0.40(25) +0.29(0)				a
Cyclohexane	+0.69(40)	+0.58(30) +0.49(6) +0.58(30) +0.58(27) +0.58(25) +0.67(45)	+0.40(22) +0.65(70) +0.50(60) +0.35(50)		+0.39(22)	a, e, f, g, h
Benzene	0.0 (25)	+0.03(25)	+0.09(25)	+0.27(25)	+0.18(25)	i
Toluene	−0.06(20) −0.11(25)	−0.06(25) −0.07(25)		+0.26(25)		a, g

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18) J. Singh and G. C. Benson, *Can. J. Chem.*, **46**, 1249, 2065 (1968).

TABLE A (Continued)

Second component	Excess volume for equimolar mixture $(V^E)_{x_1=x_2}$ (ml/mol)					Reference
	MeOH	EtOH	*n*-PrOH	*i*-PrOH	*n*-BuOH	
		−0.13(17)				
		−0.07(25)				
		+0.03(45)				
o-Xylene		−0.04(25)				g
m-Xylene		+0.02(25)				g
		+0.12(45)				
p-Xylene		−0.03(25)				g
		+0.07(45)				
Acetone	−0.35(25)	−0.05(25)	−0.04(20)	+0.24(25)	+0.06(25)	a, j
	−0.40(25)			+0.29(25)		
Acetic acid		−2.57(25)				a
n-Butyric acid		−0.61(−)				a
Ethyl acetate	−0.08(25)	+0.13(25)	+0.24(25)			a, k
		+0.19(25)				
		+0.09(0)				
Diethyl ether	−0.76(25)	−0.51(25)	−0.62(25)			a
		−0.59(0)				
		−0.55(0)				
Isopropyl ether				−0.51(25)		a
Dioxane	−0.27(22)	−0.02(30)			+0.29(25)	a
	−0.28(25)	−0.03(25)				
Phenol	−0.73(20)					a, l
	−0.79(30)					
	−0.83(40)					
Anisol	−0.20(25)	+0.10(25)				a
Chloroform	−0.15(25)	−0.19(25)		+0.02(25)		a, k
Carbon tetrachloride	−0.04(25)	−0.05(25)	−0.10(25)		−0.07(25)	a, m
Methyl iodide		+0.38(25)	+0.42(25)			a
Ethylene dichloride	0.0 (30)	+0.10(30)	+0.32(30)		+0.4 (30)	a
	0.0 (40)	+0.18(40)	+0.22(40)		+0.3 (40)	
Carbon disulfide		+0.49(30)				a
		+0.38(6)				
Dimethylsulfoxide	−0.60(25)					n
Isopropylamine				−1.32(25)		j
Triethylamine	−2.23(25)	−1.92(25)	−2.02(25)		−2.06(25)	o
Acetonitrile		−0.15(20)				a, j
		−0.01(25)				
Propionitrile				+0.26(25)		j
Aniline	−0.92(20)	−0.51(16.3)				a, l
	−1.07(30)	−0.75(25)				
	−1.34(40)	−0.83(25)				
	−0.89(25)					

TABLE A (Continued)

Second component	Excess volume for equimolar mixture $(V^E)_{x_1=x_2}$ (m*l*/mol)					Reference
	MeOH	EtOH	*n*-PrOH	*i*-PrOH	*n*-BuOH	
Pyridine		−0.37(25)				a, p
		−1.31(25)	−0.29(25)		−0.19(25)	
2,4-Lutidine		−0.96(25)				a
Quinoline		−0.5 (25)				a
Nicotine	−1.0 (20)	−0.8 (20)				a
Ethylene chlorohydrin		−0.17(20)			−0.07(25)	a
		−0.18(60)				
Formamide	−0.73(25)	−0.41(25)	−0.23(25)		−0.36(25)	a
	−0.85(40)					
Nitrobenzene	−0.4 (25)	−0.5 (25)				a

* Figures in parentheses indicate the temperature in °C.

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