

DENSITIES OF SOLUTIONS OF FOUR FLUOROALCOHOLS IN WATER

C. H. ROCHESTER AND J. R. SYMONDS

Chemistry Department, The University, Nottingham (Great Britain)

(Received June 13, 1973)

SUMMARY

Densities of aqueous solutions of four fluoroalcohols have been measured. Apparent and partial molar volumes of the alcoholic components and the excess volumes of mixing have been calculated, and are compared with the corresponding results for alkanols. A linear correlation exists between the volumes and heat capacities of transfer of alcohols from the pure liquids to aqueous solution at infinite dilution. The lines differ for alkanols and fluoroalcohols. Solute-solvent interactions involving fluoroalcohols and water and involving alkanols and water have a different influence on the structural organization of water molecules adjacent to the alcohol solute.

INTRODUCTION

The partial molar volumes of alkanols at infinite dilution in water are less than the molar volumes of the corresponding pure liquid alcohols¹⁻³. The formation of highly aqueous solutions of alcohols is accompanied by a contraction in volume which depends upon the ability of alcohol molecules to occupy cavities in the three-dimensional structure of water and upon the structuring of water molecules adjacent to the solute species. The influence which the size and shape of the alkyl groups has on the volume changes has been emphasized¹⁻³. Analogies have been drawn between the results for alcohols and for hydrocarbons, and it has been suggested that significant contributions to the volume changes arise because of "hydrophobic hydration" of the alkyl groups^{1,4}. The excess volumes of mixing of alkanols and water remain negative over the entire range of solvent composition, although the explanation of the results for solutions rich in alcohol must differ from that for the water-rich end of the scale²⁻⁴. Similar results have been observed for solutions of fluoroalcohols in water⁵⁻⁷, but no comparison of the volume changes for alkanols and fluoroalcohols has been attempted. This paper reports

densities of aqueous solutions of four fluoroalcohols. Volume changes on mixing were calculated in the hope that the values would give further^{8,9} information concerning solute-solvent interactions involving fluorocarbon groups and water.

EXPERIMENTAL

The fluoroalcohols and water were purified as before^{9,10}. Densities were measured using a bicapillary-type pycnometer of *ca.* 5 cm³ capacity immersed in a thermostat at 298 K and stable to within ± 0.005 K. Buoyancy corrections were applied. The densities are considered accurate to within $\pm 2 \times 10^{-5}$.

RESULTS

The densities ρ of solutions of four fluoroalcohols in water, the apparent molar volumes φ_V and the partial molar volumes \bar{V}_2 of the alcoholic components, and the excess molar volumes of mixing V^E are given in Table 1. Partial molar volumes were deduced from plots of apparent molar volume against the molality m of alcohol *via* equation (1).

$$\bar{V}_2 = \varphi_V + m(\partial\varphi_V/\partial m)_{T, P, n_1} \quad (1)$$

The partial molar volumes \bar{V}_2^0 of the alcohols in water at infinite dilution were deduced by extrapolation of φ_V and V_2 to zero molality of alcohol, and by consideration of the slopes as $m \rightarrow 0$ of plots of the volumes of solution containing 1 kg of water against molality. The values are compared with the molar volumes V_2^0 of the pure liquid alcohols in Table 2. Densities (which are in good agreement with the results given here) of aqueous solutions of trifluoroethanol and hexafluoropropanol have been reported by Murto *et al.*^{5,6} and were incorporated into the calculation of \bar{V}_2^0 for these two alcohols. The calculated partial molar volumes of trifluoroethanol were consistent with the published values⁶. However, the agreement for hexafluoropropanol is less satisfactory. In particular, calculations using the published densities gave no evidence for the large increase in \bar{V}_2 reported⁵ for decreasing concentrations of hexafluoropropanol at < 0.009 mole fraction. The value of $(\bar{V}_2^0 - V_2^0)$ for 2,2,3,3-tetrafluoropropan-1-ol was deduced from the density data for this alcohol given by Gajnos⁷. For comparison with the present results, the excess volumes of mixing with water of ethanol, propan-1-ol and propan-2-ol were evaluated from the appropriate density data¹¹.

The volume changes accompanying the transfer of 1 mol of the alcohols to aqueous solution at infinite dilution are compared in Table 2 with the corresponding changes in free energy, enthalpy, entropy and heat capacity. Free energies and entropies were deduced from thermodynamic data for the vaporization¹⁰ and hydration⁸ of the fluoroalcohols. Standard free energies of vaporization (and

TABLE 1

DENSITY AND VOLUME DATA FOR FLUOROALCOHOL-WATER MIXTURES AT 298 K

Mole fraction	$\rho/\text{g cm}^{-3}$	$\phi_V/\text{cm}^3 \text{ mol}^{-1}$	$\bar{V}_2/\text{cm}^3 \text{ mol}^{-1}$	$-\bar{V}^E/\text{cm}^3 \text{ mol}^{-1}$
<i>(a) 2,2,2-Trifluoroethanol</i>				
0.0365	1.06117	65.47	66.01	0.25
0.0661	1.10279	66.24	68.17	0.40
0.130	1.16686	68.11	70.40	0.55
0.188	1.20925	69.03	71.03	0.62
0.271	1.25475	69.76	71.38	0.69
0.354	1.28551	70.42	71.74	0.67
0.519	1.32737	71.19	72.12	0.58
0.645	1.34837	71.59	72.13	0.47
0.773	1.36385	71.92	72.42	0.31
1.000	1.38335	72.32	72.32	0.00
<i>(b) 2,2,3,3-Pentafluoropropan-1-ol</i>				
0.00183	1.00319	89.45	89.70	0.02 _s
0.00219	1.00455	88.01	88.29	0.03 _s
0.00290	1.00673	89.37	89.67	0.04
0.00452	1.01193	89.79	90.19	0.06
0.00633	1.01768	89.99	90.48	0.08
0.0103	1.03017	89.98	90.60	0.14
0.585	1.40788	102.84	103.07	0.24
0.717	1.42735	102.98	103.20	0.20
1.000	1.45322	103.25	103.25	0.00
<i>(c) 1,1,1-Trifluoropropan-2-ol</i>				
0.00124	0.99940	80.20	80.80	0.01 _a
0.00225	1.00106	81.87	82.47	0.02 _s
0.00663	1.00839	82.66	83.34	0.05 ₇
0.0118	1.01655	83.19	83.95	0.09 _s
0.0290	1.04200	83.25	84.42	0.23
0.447	1.21268	90.01	91.23	0.57
0.523	1.22167	90.30	91.12	0.51
0.694	1.23544	90.82	91.17	0.32
0.786	1.24055	90.95	91.30	0.26
1.000	1.24962	91.28	91.28	0.00
<i>(d) 1,1,1,3,3,3-Hexafluoropropan-2-ol</i>				
0.0172	1.06295	94.25	91.17	0.18
0.0288	1.09969	95.92	98.84	0.25
0.0438	1.14112	97.08	100.00	0.33
0.0670	1.19628	98.51	101.24	0.41
0.0919	1.24508	99.36	101.86	0.48
0.121	1.29308	99.93	102.02	0.56
0.181	1.36402	101.13	103.05	0.62
0.295	1.45371	101.99	103.69	0.76
0.531	1.53932	103.51	104.70	0.56
0.720	1.57350	104.11	104.57	0.33
1.000	1.60703	104.56	104.56	0.00

hence ΔS_{vap}^0 since ΔH_{vap}^0 are known¹⁰) were evaluated *via* the Antoine equations for each alcohol using Berthelot's equation of state to represent the non-ideality of the alcohols in the gas phase. The constants of the Antoine equation and empirical critical constants have been reported previously¹⁰. The free energies and entropies of solution of the liquid alcohols are not strictly standard changes because the hydration data⁸ used in their calculation was not corrected for the non-ideality of a pressure of alcohol vapour tending to zero in water vapour at its saturation vapour pressure.

DISCUSSION

The volume changes $\Delta V^0 = (\bar{V}_2^0 - V_2^0)$ for the transfer of alkanol molecules from the pure liquid to aqueous solution at infinite dilution are an approximately linear function of the molar volumes of the liquid alcohols. The relationship is illustrated by Figure 1, in which the present data for five fluoroalcohols have been included for comparison. For comparable molar volumes, the decrease in volume on transfer to water is greater for the fluoroalcohols than for hydrocarbon alcohols. One explanation would be that the fluoroalkyl group/water interaction is an enhanced form of the same type of interaction which occurs in hydrocarbon-water systems. This would be compatible with the suggestion⁹ that the hydration of CF_3 or CF_2 groups is more exothermic than the hydration of CH_3 or CH_2 groups respectively, despite the enthalpy changes for the transfer of four fluoroalcohols (Table 2) being less exothermic than the changes for transfer of the corresponding alkanols¹². However, the relative values of the heat capacities of hydration of

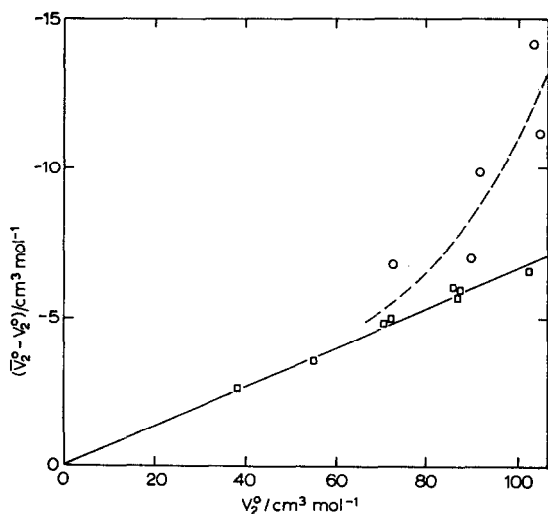


Fig. 1. The relationship between $(\bar{V}_2^0 - V_2^0)$ and V_2^0 for hydrocarbon alcohols \square (values at 298 K interpolated from data in ref. 1) and fluoroalcohols \circ .

TABLE 2
THE THERMODYNAMICS OF TRANSFER OF FIVE FLUOROALCOHOLS FROM THE PURE LIQUID TO AQUEOUS SOLUTION AT INFINITE DILUTION AND 298 K*

Fluoroalcohol	$(\bar{V}_2^0 - V_2^0)/\text{cm}^3 \text{ mol}^{-1}$	$\Delta G/\text{kJ mol}^{-1}$	$\Delta H^\circ/\text{kJ mol}^{-1}$	$\Delta S/\text{J K}^{-1} \text{ mol}^{-1}$	$\Delta C_p^\circ/\text{J K}^{-1} \text{ mol}^{-1}$
2,2,2-Trifluoroethanol	-6.8 ± 0.3	5.65	-6.11	-39.4	145
2,2,3,3-Tetrafluoropropan-1-ol	-7.0 ± 0.4	7.18	-4.36	-38.7	152
2,2,3,3,3-Pentafluoropropan-1-ol	-14.2 ± 0.3	7.46	-7.48	-50.1	231
1,1,1-Trifluoropropan-2-ol	-9.9 ± 0.5	6.76	-8.75	-52.0	199
1,1,1,3,3,3-Hexafluoropropan-2-ol	-11.2 ± 0.3	6.02	-15.53	-72.2	206

* Data for ΔH° and ΔC_p° taken from ref. 9.

gaseous fluoroalcohols and alkanols are inconsistent with the idea that fluorocarbon and hydrocarbon groups exert the same kind of influence on water structure⁸. The standard heat capacities of transfer of liquid alkanols to aqueous solution at infinite dilution^{12,13} are a linear function (Fig. 2) of the volumes of solution ($\bar{V}_2^0 - V_2^0$)^{1,14} which shows that there is a good correlation between heat capacity and volume effects in this context. A similar correlation exists (Fig. 2) for the fluoroalcohols, although there is an appreciable deviation between the lines for the two types of alcohol. The volume and heat capacity data are in accord with the proposal⁸ that solute-solvent interactions between water molecules and fluorine atoms promote a three-dimensional distorted ice-like structure around a fluoroalcohol molecule in aqueous solution. The arrangement of water molecules around a fluoroalkyl group is considered to be more compact than around a hydrocarbon group because stronger solute-solvent interactions cause the cavities occupied by the host molecules to be smaller (in proportion to the size of the solute species) for the former and because of the distortion of the orientated water structure around a fluoroalcohol. The latter effect also causes an increase in the partial molar heat capacity of a fluoroalcohol in water⁸ because the distorted structure is more easily destroyed by raising the temperature.

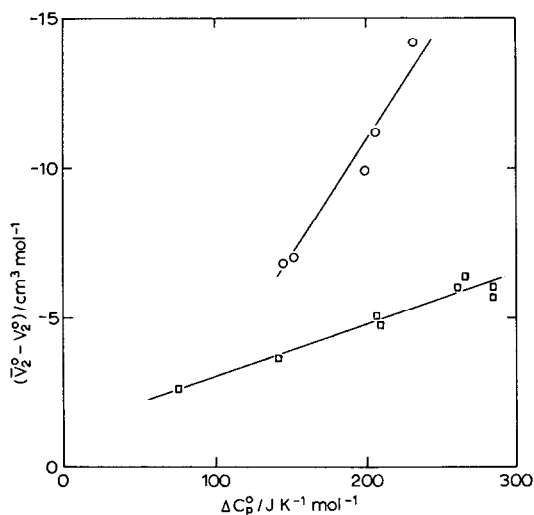


Fig. 2. The relationship between $(\bar{V}_2^0 - V_2^0)$ and ΔC_p^0 for hydrocarbon alcohols \square and fluoroalcohols \circ .

The excess volumes of mixing of the four fluoroalcohols with water are negative over the entire miscible ranges of liquid composition. In accord with the more negative $(\bar{V}_2^0 - V_2^0)$ values for fluoroalcohols, V^E is more negative than for alkanols at the highly aqueous end of the composition scale. However, at all other alcohol concentrations V^E is less negative, and the minima in the curves occur at

lower alcohol mole fractions for the fluoroalcohols. Similar results have been recorded for 2,2,3,3-tetrafluoropropan-1-ol⁷. Calculations for this alcohol show that, as for three other fluoroalcohols (Table 1), the partial molar volume of the alcohol in highly alcoholic mixtures with water is greater than the molar volume of the pure alcohol. The negative V^E values for solutions of these four fluoroalcohols must therefore be compatible with partial molar volumes of water in dilute solutions of water in the alcohols, which are appreciably less than the molar volume of liquid water. The same conclusion is justifiable for pentafluoropropan-1-ol (Table 1). The structure of water is destroyed when the liquid is dissolved in an alcohol⁴. Strong specific hydrogen-bonding interactions involving the comparatively acidic fluoroalcohols as hydrogen-bond donors and water as acceptor molecules are thought to exist in the solutions. Similar interactions probably occur in solutions of water in alkanols, despite a statistical factor which doubles the probability of an alcohol molecule behaving as an acceptor rather than as a donor⁴. Thus, for example, methanol is a stronger acid than water in methanol/water mixtures, the difference in acidity becoming greater with increasing methanol content^{15,16}. Fluoroalcohols are stronger acids than alkanols¹⁷ and therefore it might be expected that V^E should be more negative for the former. This is the reverse of the experimental result, and suggests that there is some steric factor which reduces the number of fluoroalcohol/water interactions. The interactions are stronger than for alkanol-water systems but there may be fewer of them. This is consistent with the lesser extent of molecular association for fluoroalcohols in the pure liquids^{18,19}. A similar explanation has been used to account for the observed enthalpies of mixing of alcohol-rich mixtures of a series of increasingly bulky alkanols with water⁴.

ACKNOWLEDGEMENTS

The authors thank Unilever Ltd. for financial assistance.

REFERENCES

- 1 M. E. FRIEDMAN AND H. A. SHERAGA, *J. Phys. Chem.*, **69** (1965) 3795.
- 2 K. NAKANISHI, N. KATO AND M. MARUYAMA, *J. Phys. Chem.*, **71** (1967) 814.
- 3 K. NAKANISHI, *Bull. Chem. Soc. Jap.*, **33** (1960) 793.
- 4 F. FRANKS AND D. J. G. IVES, *Quart. Rev. Chem. Soc.*, **20** (1966) 1.
- 5 J. MURTO, A. KIVINEN, S. KIVIMAA AND R. LAAKSO, *Suomen Kem.*, **B40** (1967) 250.
- 6 J. MURTO AND E.-L. HEINO, *Suomen Kem.*, **B39** (1966) 263.
- 7 G. E. GAJNOS, *Ph. D. Thesis*, University of Pennsylvania, 1965.
- 8 C. H. ROCHESTER AND J. R. SYMONDS, *J. Chem. Soc., Faraday Trans. I*, **69** (1973) 1577.
- 9 C. H. ROCHESTER AND J. R. SYMONDS, *J. Chem. Soc., Faraday Trans. I*, **69** (1973) 1274.
- 10 C. H. ROCHESTER AND J. R. SYMONDS, *J. Chem. Soc., Faraday Trans. I*, **69** (1973) 1267.
- 11 K.-Y. CHU AND A. R. THOMPSON, *J. Chem. Eng. Data*, **7** (1962) 358; *International Critical Tables*, McGraw-Hill, New York, Vol. 3, 1928, p. 116.
- 12 D. M. ALEXANDER AND D. J. T. HILL, *Aust. J. Chem.*, **22** (1969) 347.

- 13 E. M. ARNETT, W. B. KOVER AND J. V. KOVER, *J. Amer. Chem. Soc.*, *91* (1969) 4028.
- 14 D. A. ARMITAGE, M. J. BLANDAMER, K. W. MORCOM AND N. C. TRELOAR, *Nature (London)*, *219* (1968) 718.
- 15 C. H. ROCHESTER, *J. Chem. Soc., Dalton Trans.*, (1972) 5.
- 16 G. H. PARSONS AND C. H. ROCHESTER, *J. Chem. Soc., Faraday Trans. I*, *68* (1972) 523.
- 17 C. H. ROCHESTER, in S. PATAI (Ed.), *The Chemistry of the Hydroxyl Group*, Interscience, London, 1971, p. 327.
- 18 A. KIVINEN AND J. MURTO, *Suomen Kem.*, *B40* (1967) 6.
- 19 A. KIVINEN, J. MURTO, J. KORPPI-TOMMOLA AND R. KUOPIO, *Acta Chem. Scand.*, *26* (1972) 904.