pendency of these limiting activity coefficients at different temperature levels can be conveniently incorporated in order to evaluate the temperature dependency of the group-interaction parameters by the SUPERFAC model for the activity coefficient (*16*).

Registry No. Sulfolane, 126-33-0; cyclohexane, 110-82-7; hexane, 110-54-3; heptane, 142-82-5.

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Excess Molar Volumes of 1-Alkanol (C_1–C_5) Binary Mixtures with Acetonitrile

Jagjit S. Sandhu,* Ashok K. Sharma, and Ramesh K. Wadi†
Department of Chemistry, Punjabi University, Patiala 147 002, India

Excess molar volumes (V^E) for binary mixtures containing acetonitrile and a 1-alkanol (C_1–C_5) measured dilatometrically at 308.15 K are reported over the entire range of compositions. Equimolar excess volumes increase linearly with increase in the number of carbon atoms in the hydrocarbon chain. The V^E–x curve is skewed toward low acetonitrile mole fraction for ethanol to 1-pentanol. The results are rationalized in terms of the physical and specific interactions in these mixtures.

Introduction

Acetonitrile, 1-alkanols (C_1–C_5), and their binary mixtures are frequently used as solvents in chemistry and modern technology (*1*, *2*). We report here the excess molar volumes for methanol (MeOH) + acetonitrile (AN), ethanol (EtOH) + AN, 1-propanol (PrOH) + AN, 1-butanol (BuOH) + AN, and 1-pentanol (AmOH) + AN mixtures at 308.15 K and over the whole mole fraction range measured by using a continuous dilution dilatometer.

Experimental Section

Benzene (B.D.H., AnalaR), cyclohexane (Glaxo, L.R.), acetonitrile (E. Merck), methanol (B.D.H., AnalaR), ethanol (Bengal Chemicals, dehydrated), and 1-propanol (Riedel) were purified by recommended methods (*3*, *4*). Purity of the solvents was ascertained by the constancy of their boiling temperatures during final distillations and also by comparing their densities, determined by a pycnometric technique with the corresponding literature values (Table I). Mercury needed for calibrations and used for use in the dilatometer was purified first by washing several times with 5% nitric acid and then with water till free from acid. It was then dried and distilled under partial vacuum. Due to its contact with the liquids in the dilatometer, mercury required purification afterone complete experiment.

Table I. Densities of Pure Liquids at 308.15 K

component	ρ, g cm^{-3} this study	ρ, g cm^{-3} lit. (*3*, *4*)
acetonitrile	0.7656	0.7659
benzene	0.8629	0.8630
1-butanol	0.7982	0.7987
cyclohexane	0.7644	0.7644
ethanol	0.7766	0.7768
methanol	0.7772	0.7770
1-pentanol	0.8039	0.8041
1-propanol	0.7918	0.7916

A continuous dilution dilatometer was used for volume measurements (*5*). Temperature of the measurements was controlled to within ±0.01 K. The procedural details of the method are practically the same as described by earlier workers. The mole fractions and the excess volumes are believed to be precise to within ±0.0002 and ±0.005 cm^3 mol^{-1}, respectively. Working of the dilatometer was checked by measuring V^E of benzene + cyclohexane mixtures as recommended by the previous workers (*6*, *7*). Our equimolar V^E value at 298.15 K was 0.644 cm^3 mol^{-1} as compared to the literature (*7*) value of 0.6496 cm^3 mol^{-1}. The deviations from the corresponding literature values at other mole fractions were within ±0.01 cm^3 mol^{-1}.

Results and Discussion

The V^E values for MeOH + AN, EtOH + AN, PrOH + AN, BuOH + AN, and AmOH + AN at 308.15 K and over the whole mole fraction range are given in Table II. The composition dependence of V^E was correlated by the polynomial (*1*)

$$V^E/(\text{cm}^3\ \text{mol}^{-1}) = x(1-x)\sum_{i=0}^{R} v_i(2x-1)^i \qquad (1)$$

where x is the mole fraction of acetonitrile. The estimates of the parameters v_i were obtained by the method of least squares and are collected in Table III. The deviations δV^E of the experimental values from the calculated (least squares) ones

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† Present address: Department of Chemistry, University of Delhi, Delhi, India.

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Table II. Excess Molar Volumes (V^E) at 308.15 K

x	V^E, cm^3 mol^{-1}	δV^E, cm^3 mol^{-1}
	$(1-x)CH_3OH + xCH_3CN$	
0.0213	−0.005	0.009
0.0747	−0.043	0.002
0.1241	−0.065	0.003
0.1874	−0.088	0.004
0.2316	−0.100	0.005
0.3039	−0.118	0.001
0.3420	−0.124	0.000
0.3910	−0.129	−0.002
0.4071	−0.136	−0.008
0.4433	−0.136	−0.008
0.4910	−0.124	0.001
0.4988	−0.127	−0.003
0.5481	−0.116	0.003
0.5856	−0.114	0.001
0.6756	−0.090	0.005
0.7358	−0.071	0.009
0.8581	−0.051	−0.006
0.9433	−0.017	0.001
	$(1-x)C_2H_5OH + xCH_3CN$	
0.1312	0.042	0.001
0.2229	0.055	−0.002
0.2900	0.064	−0.002
0.3364	0.071	−0.001
0.3827	0.078	0.000
0.4561	0.093	0.004
0.5634	0.107	0.003
0.5643	0.103	0.001
0.6207	0.111	0.000
0.6872	0.113	−0.003
0.7315	0.114	−0.002
0.7988	0.108	−0.002
0.8608	0.095	0.002
0.9467	0.052	0.005
	$(1-x)n\text{-}C_3H_7OH + xCH_3CN$	
0.0549	0.011	−0.003
0.0883	0.011	−0.001
0.1367	0.021	0.001
0.1627	0.026	0.002
0.2201	0.036	0.002
0.2393	0.037	0.000
0.3026	0.048	0.001
0.3604	0.051	−0.005
0.4060	0.060	−0.002
0.4237	0.060	−0.004
0.4709	0.069	0.000
0.4740	0.066	−0.003
0.4778	0.071	−0.001
0.4785	0.072	0.002
0.4986	0.071	−0.001
0.5250	0.072	−0.002
0.5468	0.078	0.003
0.5539	0.077	0.001
0.5573	0.075	−0.001
0.6017	0.082	0.005
0.6119	0.081	0.004
0.6544	0.079	0.002
0.7213	0.068	−0.004
0.7723	0.059	−0.007
0.7934	0.067	0.004
0.8445	0.057	0.004
0.8679	0.047	0.000
0.8786	0.044	0.000
0.9113	0.031	−0.003
0.9435	0.023	0.000
0.9600	0.017	0.000
	$(1-x)n\text{-}C_4H_9OH + xCH_3CN$	
0.0659	0.008	−0.002
0.2012	0.036	−0.004
0.2628	0.060	0.004
0.3086	0.067	0.000
0.3628	0.081	0.001
0.4332	0.095	0.000
0.4911	0.104	0.000
0.4995	0.109	0.003
0.5490	0.110	−0.001
0.5589	0.114	0.002
0.6056	0.110	−0.004
0.6184	0.115	0.001
0.6526	0.110	−0.004
0.6896	0.112	0.001
0.7421	0.104	0.000
0.7923	0.093	0.000
0.8634	0.074	0.003
0.9336	0.040	0.001
0.9772	0.014	0.000
	$(1-x)n\text{-}C_5H_{11}OH + xCH_3CN$	
0.0410	0.031	0.004
0.1181	0.062	0.000
0.1941	0.084	−0.001
0.2678	0.093	−0.006
0.3327	0.106	−0.001
0.3928	0.115	0.003
0.4655	0.120	0.002
0.5016	0.123	0.003
0.5526	0.125	0.003
0.5551	0.123	0.001
0.6177	0.123	−0.001
0.7009	0.117	−0.005
0.7793	0.105	−0.007
0.8363	0.092	−0.001
0.8925	0.080	−0.005
0.9406	0.054	0.011
0.9764	0.031	0.010

Table III. Parameters v_i of Eq 1 and Standard Deviations $\sigma(V^E)$ at 308.15 K

mixture	N	v_0	v_1	v_2	$\sigma(V^E)$, cm^3 mol^{-1}
$(1-x)CH_3OH + xCH_3CN$	18	−0.4958	0.1753		0.005
$(1-x)C_2H_5OH + xCH_3CN$	14	0.3799	0.2925	0.3570	0.003
$(1-x)n\text{-}C_3H_7OH + xCH_3CN$	31	0.2879	0.1643		0.003
$(1-x)n\text{-}C_4H_9OH + xCH_3CN$	19	0.4231	0.2689	−0.0378	0.003
$(1-x)n\text{-}C_5H_{11}OH + xCH_3CN$	17	0.4785	0.1106	0.3529	0.006

are included in Table II, whereas the standard deviations $\sigma(V^E)$ calculated as

$$\sigma(V^E) = \{\sum(\delta V^E)^2/(N-R-1)\}^{1/2} \qquad (2)$$

where N is the total number of observations and R the degree of polynomial used for the best fit, are given in Table III. The V^E values are plotted against x in Figure 1. Some of the (V^E, x) points are omitted to avoid congestion of points. It is clear from Table II and Figure 1 that the V^E for methanol mixture is negative over the entire composition range, whereas it is positive for rest of the mixtures. The V^E–x curve is skewed toward low mole fraction of acetonitrile for MeOH + AN (x_{min} = 0.44). For other mixtures V^E–x curves are skewed toward high x values (x_{max} = 0.55–0.73). The equimolar V^E values (Table III) lie in the order MeOH < PrOH < EtOH < BuOH < AmOH. These are plotted vs. n, the number of carbon atoms in the alkanol chain, in Figure 2. The $V^E(x=0.5)$ for H_2O + AN at 308 K, calculated from its values at 279 and 298 K (*13*) and assuming the temperature dependence of V^E to be linear, is also plotted in Figure 2 for comparison. Thus the curve represents the change in excess volume at x = 0.5 and at 308

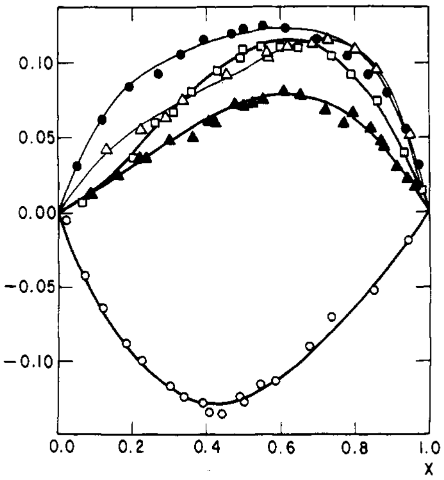

Figure 1. Excess molar volumes V^E (308.15 K) of acetonitrile mixtures with ○, CH_3OH; △, C_2H_5OH; ▲, n-C_3H_7OH; □, n-C_4H_9OH; ●, n-$C_5H_{11}OH$.

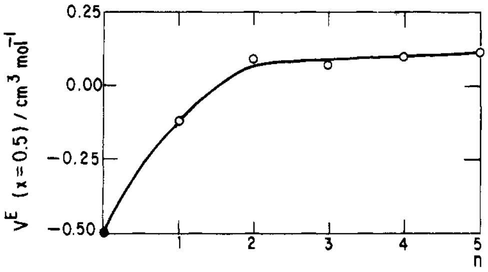

Figure 2. Equimolar V^E (308.15 K) plotted vs. number of carbon atoms (n) in 1-alkanol: ●, H_2O + CH_3CN; ○, n-$C_nH_{2n+1}OH$ + CH_3CN.

K for various mixtures obtained by replacing H in H_2O + AN by successive n-alkyl groups. It can be seen that the curve has curvature upto $n = 2$ and is a line thereafter. Therefore, the $V^E(x=0.5)$ for C_2–C_5 1-alkanol mixtures with AN can be represented by eq 3 with a standard deviation $\sigma = 0.015$ cm^3

$$V^E(x=0.5)/(\text{cm}^3\ \text{mol}^{-1}) = 0.06 + 0.011n \qquad (3)$$

mol^{-1}. The V^E of mixing of $-OH$ and $-CH_2$ groups with acetonitrile are 0.06 and 0.011 cm^3 mol^{-1}, respectively. Obviously, eq 3 can be used to predict $V^E(x=0.5)$ values for mixtures of higher n-alkanols with AN.

The observed V^E can be considered as arising from two types of interactions between the components: (1) physical interaction consisting mainly of dispersion forces and making a positive contribution, and (2) chemical or specific interaction resulting in a volume decrease. The latter includes charge-transfer forces, forming and/or breaking of H bonds and other complex forming interactions. It is well-known that both acetonitrile and 1-alkanols are associated in liquid state. Acetonitrile contains molecules with strong parallel and antiparallel orientations and this strongly ordered structure is stabilized by dipole–dipole interactions (*8*), whereas 1-alkanols are associated through the hydrogen bonding of their hydroxyl groups. Association decreases with increase in molar mass of 1-alkanol (*9*–*12*). The increase in V^E with the increase in molar mass of 1-alkanol implies that acetonitrile–1-alkanol interaction is relatively weaker. Therefore, the negative V^E in the case of MeOH + AN results because the decrease in volume due to the fitting in of acetonitrile molecules in the H-bonded network of MeOH overweighs the total increase in volume due to physical interactions and to the breaking up of MeOH structure by acetonitrile. Assuming the positive contribution due to H-bond breaking to be constant, the observed increase in V^E with increase in molar mass of 1-alkanol can be rationalized.

The skewness of V^E–x curves for these mixtures is due to the difference in component molar volumes and to the presence of specific interactions, the position of the extremum exhibiting the net effect. It is interesting to compare 1-alkanol + AN with H_2O + AN (*13*) for which V^E (298.15 K) is minimum (−0.56 cm^3 mol^{-1}) at $x = 0.33$. Our mixtures are H_2O + AN in which one H of H_2O is replaced by CH_3, C_2H_5, n-C_3H_7, n-C_4H_9, or n-C_5H_{11}. The extremum occurs at $x = 0.44$, 0.77, 0.60, 0.61, and 0.55, respectively. It is clear that an increase in hydrophobicity of 1-alkanol results in the shift of extremum toward higher mole fraction of acetonitrile. The maximum at $x \simeq 0.6$ in the case of PrOH, BuOH, and AmOH indicates that if H bonding is assumed to be constant in these alkanols, then even an increase in the difference in molecular size of the two components does not change the position of the maximum.

Registry No. MeCN, 75-05-8; MeOH, 67-56-1; EtOH, 64-17-5; PrOH, 71-23-8; BuOH, 71-36-3; 1-pentanol, 71-41-0.

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Solubility Relations in the System Potassium Chloride–Ferrous Chloride–Water between 25 and 75 °C at 1 atm

I-Ming Chou* and Luong D. Phan

U.S. Geological Survey, 959 National Center, Reston, Virginia 22092

Solubility relations in the ternary system KCl–$FeCl_2$–H_2O have been determined by means of the visual polythermal method at 1 atm from 18 to 75 °C along 10 composition lines. Solubilities of sylvite were measured along five composition lines defined by mixing KCl with five aqueous $FeCl_2$ solutions containing 10, 20, 30, 38, and 45 wt % of $FeCl_2$, respectively. Solubilities of $FeCl_2 \cdot 4H_2O$ were also determined along five composition lines defined by mixing $FeCl_2 \cdot 4H_2O$ with five aqueous KCl solutions containing 5, 10, 14.98, 19.97, and 24.99 wt % KCl, respectively. The maximum uncertainties in these measurements are ±0.02 wt % in KCl, ±0.15 wt % in $FeCl_2$, and ±0.15 °C. The data along each composition line were regressed to a smooth curve. The maximum deviations of the measured solubilities from the smoothed curves are 0.22 wt % in KCl and 0.12 wt % in $FeCl_2$. Isothermal solubilities of sylvite and $FeCl_2 \cdot 4H_2O$ were calculated from these smoothed curves at 25, 40, 50, 60, 70, and 75 °C.

Introduction

Hydrated ferrous chloride is an occasional phase found together with halite and/or sylvite in fluid inclusions in quartz in pegmatites (e.g., Naumov and Shapenko (*1*)) and in porphyry systems (e.g., Grant et al. (*2*)). Two potassium iron chloride phases, which have possible compositions of $KFeCl_{3-4} \cdot nH_2O$ and $KFe_2Cl_{5-7} \cdot mH_2O$ determined by means of SEM/energy dispersive analyses on opened high salinity fluid inclusions from a porphyry copper deposit, were reported by Quan et al. (*3*). The oxidation state of iron in these phases has not been determined. Also, the data on solubility of iron chloride in hydrothermal brines are lacking. Solubility relations in the system $NaCl$–$FeCl_2$–H_2O between 25 and 70 °C at 1 atm were recently reported by Chou and Phan (*4*). In this study, the solubility relations in the system KCl–$FeCl_2$–H_2O were determined at 1 atm and between 25 and 75 °C.

Experimental Section

The visual polythermal method used in this study has been