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COMPRESSIBILITY OF BINARY MIXTURES OF ASSOCIATING LIQUIDS

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This paper presents the application of ultrasonic methods to investigate the structure of liquid mixtures of polyhydroxyalcohols (glycerol-butanediol-1.3 and glycerol-2-methylpentanediol-2.4).

Measurements were carried out on the propagation of ultrasonic waves at a frequency $f = 2.5$ MHz over the temperature range 283–303 K and on density over the temperature range 273–303 K for the alcohols and mixtures.

Excess compressibilities were calculated for the systems of interest. It was shown that the compressibility of mixtures of associating liquids was determined not only by specific intermolecular interactions, but also a major role is played by steric factors (the degree of filling the space).

1. Introduction

From measurements of ultrasonic velocity and density, it is possible to determine for binary mixtures the magnitude of deviation from the properties resulting from thermodynamic ideality on the basis of the dependence of the excess adiabatic compressibility $\varkappa_S^E = -[\partial V^E/\partial p]_s$ on the mole fraction.

From the general thermodynamic criterion of the ideality of a mixture [1], $\bar{G}^{\rm id} = \sum x_i \mu_i = \sum x_i, \mu_i^0 + RT\sum x_i ln x_i$, there results (for an ideal mixture) additivity of molar volumes and enthalpies with respect to the mole fraction: $\bar{V}^{\rm id} = \sum x_1 V_i^0$, $\bar{H}^{\rm id} = x_i H_i^0$, where x_i, μ_i^0, V_i^0 and H_i^0 are respectively mole fractions, chemical potentials, molar volumes and enthalpies of pure component; whereas $\bar{G}^{\rm id}$, $\bar{V}^{\rm id}$ and $\bar{H}^{\rm id}$ are the corresponding mean molar quantities for an ideal mixture. Hence, taking, after ROTHHARDT's proposal [2], enthalpy as the basic thermodynamic potential, for an ideal binary mixture

$$\bar{H}^{\rm id} = x_1 H_1^0 + x_2 H_2^0,$$

$$\bar{\varkappa}^{\rm id} = \left(\frac{\partial^2 \bar{H}^{\rm id}}{\partial p^2}\right)_{\bar{s}} = x_1\left(\frac{\partial^2 \bar{H}_1^0}{\partial p^2}\right)_{\bar{s}} + x_2\left(\frac{\partial^2 H_2^0}{\partial p^2}\right)_{\bar{s}} = x_1\left(\frac{\partial V_1^0}{\partial p}\right)_{\bar{s}} + x_2\left(\frac{\partial V_2^0}{\partial p}\right)_{\bar{s}}. \qquad (1.1)$$

Assuming that

$$\left(\frac{\partial^2 H_i^0}{\partial p^2}\right)_{\bar{s}} \approx \left(\frac{\partial^2 H_i^0}{\partial p^2}\right)_{s_i^0} = \varkappa_i^0 \tag{1.2}$$

the adiabatic compressibility of an ideal binary mixtures can be regarded as a quantity approximately additive with respect to the mole fraction

$$\varkappa^{\mathrm{id}} = x_1 \varkappa_1^0 + x_2 \varkappa_2^0. \tag{1.3}$$

The approximate character of this additivity results from the fact that $\bar{s} = \sum x_i s_i^0 - R \sum x_i \ln x_i \neq s_i^0$ and that despite the constant entropy of the whole mixture $s = \mathrm{const}$ in the process of compression and decompression, the constancy of the component entropies $s_i = \mathrm{const}$ is not ensured [3, 4].

It seems, however, that the approximation on which equation (1.3) is based, is satisfied sufficiently well for the deviation of binary mixture from thermodynamic ideality to be evaluated from excess adiabatic compressibility, defined as

$$\bar{\varkappa}_s^E = \bar{\varkappa}_s - \bar{\varkappa}_s^{\mathrm{id}} = \bar{\varkappa}_s - (x_1 \varkappa_1^0 + x_2 \varkappa_2^0). \tag{1.4}$$

2. Experimental part

Both glycerol (P.O.Ch. Gliwice, pure for analysis), 2-methylpentanediol-2.4 (BDH Chemicals Ltd., pure), and butanediol-1.3 (Koch-Light Laboratories Ltd, pure) were dehydrated by boiling under reduced pressure at a temperature of about 373 K.

The densities of mixtures and pure components were determined pycnometrically over the temperature range 273–303 K, at temperature stability of ±0.05 K. To reduce the weight in air, the relation $\varrho = \varrho' + 0.0012\ (1 - \varrho'/\varrho^0)$ was used, where ϱ – absolute density of water, ϱ' – measured density. The dependence of density on temperature can be represented by the linear equation $\varrho = AT + B$, where A and B are constants determined by the least squares method. The density equations are listed in Table 1, where r – the correlation coefficient of the linear dependence of ϱ on T; x_2 – mole fraction of the diol.

The ultrasonic wave propagation at a frequency of 2.5 MHz in the solutions under study and its changes over the temperature range 283–303 K were measured by an ultrasonic pulse-phase interferometer (produced by Institute of Fundamental Technological Research, Polish Academy of Sciences) with accuracy of ±0.05 per cent (Table 2, where x_2 – mole fraction of the diol).

Table 1

x_2	Glycerol-butanediol-1.3 ϱ [kg/m^3]	r
0.	$-6.2410\times10^{-1}T+1.4430\times10^3$	-0.9995
0.1020	$-6.0437\times10^{-1}T+1.4061\times10^3$	-0.9992
0.2035	$-6.0471\times10^{-1}T+1.3684\times10^3$	-0.9993
0.3046	$-6.2925\times10^{-1}T+1.3501\times10^3$	-0.9991
0.5054	$-6.2278\times10^{-1}T+1.2979\times10^3$	-0.9996
0.7045	$-6.2214\times10^{-1}T+1.2510\times10^3$	-0.9989
1	$-6.9167\times10^{-1}T+1.2037\times10^3$	-0.9994
	Glycerol-2-methylpentanediol-2.4	
0.0314	$-6.5545\times10^{-1}T+1.4273\times10^3$	-0.9989
0.0879	$-7.0780\times10^{-1}T+1.4173\times10^3$	-0.9996
0.1716	$-6.9645\times10^{-1}T+1.3791\times10^3$	-0.9954
0.2956	$-6.9524\times10^{-1}T+1.3282\times10^3$	-0.9960
0.4478	$-6.2032\times10^{-1}T+1.2531\times10^3$	-0.9948
0.6452	$-6.5025\times10^{-1}T+1.1981\times10^3$	-0.9317
0.8153	$-6.6247\times10^{-1}T+1.1616\times10^3$	-0.9960
1	$-6.1967\times10^{-1}T+1.1051\times10^3$	-0.9996

Table 2
u[m/s]

x_2	283.15 K	293.15 K	303.15 K
	Glycerol-butanediol-1.3		
0	1944.5	1920.1	1895.8
0.1020	1894.0	1869.6	1844.8
0.2035	1840.0	1819.3	1798.1
0.3046	1797.5	1773.7	1751.7
0.5054	1722.0	1696.2	1672.0
0.7045	1653.0	1626.4	1600.6
1	1573.0	1547.0	1519.0
	Glycerol-2-methylpentanediol-2.4		
0.0314	1906.4	1882.2	1858.2
0.0879	1850.8	1826.0	1801.3
0.1716	1781.0	1754.2	1728.4
0.2956	1667.8	1638.4	1610.0
0.4478	1568.5	1539.4	1510.5
0.6452	1470.0	1440.0	1410.0
0.8153	1411.2	1380.3	1350.0
1	1344.0	1311.0	1280.0

3. Discussion of the results and conclusions

The excess compressibilities calculated from equation (1.4) for the two systems under study: I — glycerol-butanediol-1.3 and II — glycerol-2-methylpentanediol-2.4, are shown in Figs. 1 and 2. Over the whole concentration

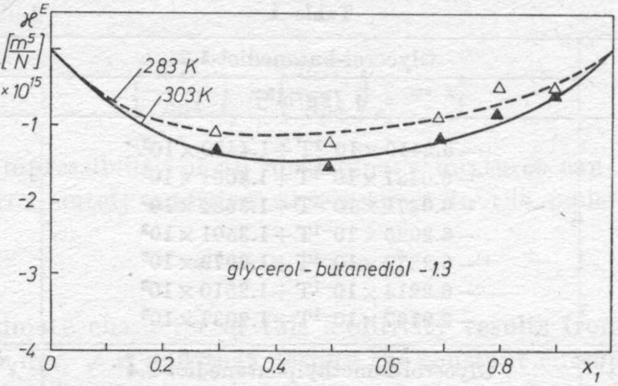


Fig. 1. Excess compressibility as a function of the mole fraction (calculated from equation (1.4)) for the glycerol-butanediol-1.3 system

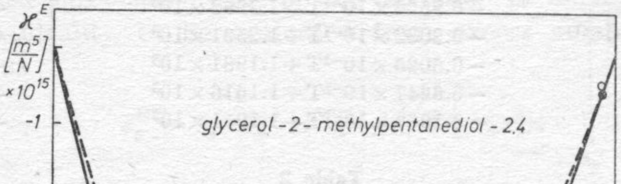


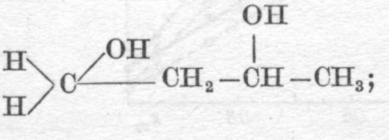
Fig. 2. Excess compressibility as a function of the mole fraction (calculated from equation (1.4)) for the glycerol-2-methylpentanediol-2.4 system

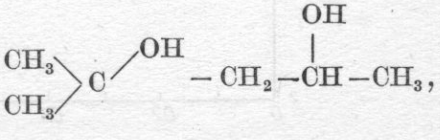
range the excess adiabatic compressibilities are negative. The components of the mixtures of interest are liquids of a high degree of association. Specific intermolecular interactions in the form of hydrogen bonds lead to the formation of incessantly disintegrating and reintegrating disturbed fragments of the crystal structure (subject to translation and not separated by discontinuity boundaries), and also determine the response to mechanical stress [5–9]. The formation of intra- and intermolecular hydrogen bonds should in the case of mixtures of polyhydric liquids lead to the formation of relatively extensive clusters (increased degree of association).

On the basis of JACOBSON's model of intermolecular free path [14], the formation of complexes between the components of a mixture was repeatedly related in the literature [10, 11] to an increase in compressibility (positive excess compressibility), with complexes (associates) considered incompressible.

However, this assumption seems to be unwarranted, particularly in the case of multimers formed by hydrogen bonds. According to KUDRYAVTSEV [12] and KUCZERA [13], the acoustic wave propagation is not only an intermolecular effect. Particularly in the case of an extensive cluster, the transmission of an acoustic pulse within the cluster must occur at finite velocity. On the assumption that the pulse transmission along a hydrogen bond is faster than on a free path, it can be shown that association should cause an increase in the phase velocity and decreased compressibility ("stiffening" of the system). It can thus be concluded that negative excess compressibilities indicate stronger association in mixtures than in pure components.

Since in the case of the two mixtures one of the components is common to both (glycerol), whereas the two diols differ only in the number of methyl groups:





similar abilities to form hydrogen bonds (association) can be expected in the two systems. However, mixture II shows much greater negative compressibility, suggesting the possibility of the free space in the openwork structure of the cluster having been "blocked" by two additional methyl groups of 2-methylpentanediol-2.4. Thus, it can be stated that the compressibility of a liquid system is determined not only by specific intermolecular interactions, but also that a major role is played by steric factors.

In the case of the two mixtures, the excess compressibilities become more and more negative with increasing temperature (Figs. 1 and 2). This indicates the formation of increasingly firm clusters (more immune to the disturbing effect of thermal motion) in the mixtures compared to the clusters which form in the pure components. Fig. 3 shows the properties of mixture II at temperatures of 283 K and 303 K, based on the dependence of the coefficients of adiabatic compressibility of a real mixture, β_s, and an ideal one, β_s^{id}, on the concentration represented in volume fractions x_{v1} of glycerol. An increase in the difference between β_s and β_s^{id} (the latter defined usually as $\beta_s^{\mathrm{id}} = \sum x_{vi}\beta_{si}$ [4]) with increasing temperature, indicates more negative excess compressibilities while for two different temperatures $T_2 > T_1$ the "absolute" compressibility of the system at the temperature T_2 is obviously greater than that at the temperature T_1 (Fig. 3).

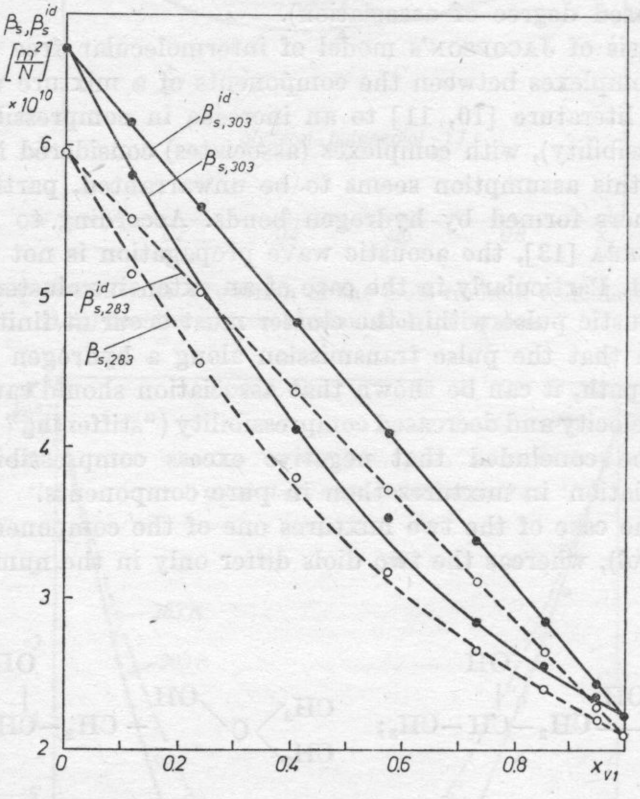


Fig. 3. The glycerol-2-methylpentanediol-2.4 system. The dependence of the coefficients of adibatic compressibility of a real mixture, β_s, and an ideal one, β_s^{id}, on the concentration, expressed in volume fractions x_{v1}, for temperatures given in the figure

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